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Second harmonic chalcone crystal: Synthesis, growth and characterization

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ABSTRACT

The novel nonlinear optical chalcone derivative (2*E*)-3-[4-(methylsulfanyl)phenyl]-1-(3-bromophenyl)prop-2-en-1-one (3Br4MSP) crystals have been grown by slow evaporation technique at ambient temperature. The crystal was subjected to different types of characterization method in order to study its possible application in nonlinear optics. The structure determination of the grown crystal was done by single crystal X-ray diffraction study. The morphology of the crystal is studied. The crystal was subjected to thermal analysis to find its thermal stability. The grown crystals were characterized for their optical transmission and mechanical hardness. The second harmonic generation (SHG) efficiency of the crystal is obtained by classical powdered technique. The laser damage threshold for 3Br4MSP crystal was determined using Q-switched Nd:YAG laser.

1. Introduction

Organic molecules especially chalcone are of particular interest over inorganic molecules in the field of nonlinear optical (NLO) applications [1]. Chalcone has π conjugated system. Due to the overlapping of π orbital, delocalization of electronic charge distribution leads to a high mobility of the electron density [2]. The presence of appropriate terminal electron donor or acceptor groups on aromatic rings can enhance the asymmetric electron distribution in either or both ground and excited electron states leading to large molecular hyperpolarizabilities and good crystallizability [3]. Chalcone crystals showing NLO properties were extensively studied by incorporating different characterization techniques. The most important crystals like 1-(4-methylphenyl)-3-(4-methoxyphenyl)-2-propen-1-one [2], 5-Br-2-thienyl-4'-methoxychalcone (5Br2ThMC) [4], 4-OCH_3-4'-nitrochalcone (MNC) [5], 3-Br-4'-methoxychalcone (3BMC) [6], etc. were studied for their possible application in the field of nonlinear optics. Quite often these molecules tend to crystallize in long needles or thin plates owing to their polar nature [7].

In order to use the crystal for high power laser applications, it should have high laser damage threshold value. The novel crystal 3Br4MSP has good laser damage threshold value, which is comparable with high quality NLO crystals. To exploit the crystal for SHG applications it is desirable to have SHG efficiency more than the reference material Urea. 3Br4MSP has SHG efficiency nearly 3 times higher than that of urea. To make the crystal suitable for device applications it should have wide transparency window. Crystal 3Br4MSP has wide transparency window starting from visible region and extending into infrared (IR) region. These qualities of the crystal 3Br4MSP make it interesting to consider for device applications. This paper deals with the growth of bromo substituted chalcone (2*E*)-3-[4(methylsulfanyl)phenyl]-1-(3-bromophenyl)prop-2-en-1-one (3Br4MSP) and its characterization by some standard techniques.

2. Experimental procedure

2.1. Synthesis and growth of the compound

Chalcone derivatives can be synthesized by Clainsen–Schmidt condensation method [3]. The AR grade chemicals without further purification were used. A mixture of equimolar quantities (0.01 mole each) of 3-bromo acetophenone and 4-methylthiobenzaldehyde in ethanol (60 ml) were stirred for 2 h in the presence of NaOH (2 ml, 30%). Then the contents of the flask were poured into ice cold water (250 ml) and left for 12 h. The resulting crude solid was collected by filtration, dried and purified by repeated crystallization from methanol. Selection of suitable solvent is very important for the growth of good quality of crystals. We observed that methanol is found to be the best solvent for this crystal growth by slow evaporation method at room temperature.

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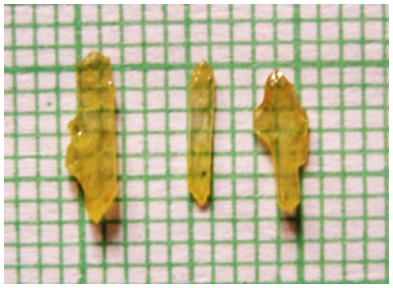

Fig. 1. Photograph of 3Br4MSP crystals.

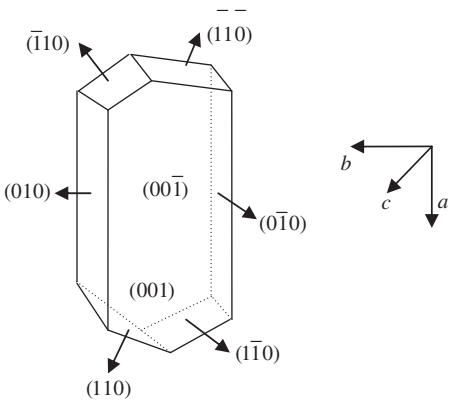

Fig. 2. Morphology of the crystal 3Br4MSP.

Tiny needle shape crystals were obtained. Good quality crystals were selected for further growth and suspended into saturated solution of the compound by maintaining constant room temperature. Well-defined transparent crystals appeared in the growth vessels within 2 weeks of solution evaporation. The crystals reached a maximum size of $7 \times 2 \times 2$ mm^3 in a period of two weeks. Crystals obtained (Fig. 1) were yellowish in color, nonhygroscopic and stable at room temperature.

To determine the morphology of the grown crystal, the faces of the crystal were indexed using Enarf CAD-4 diffractometer along with a four circle goniometer. The morphology of the crystal 3Br4MSP and its faces are shown in Fig. 2.

3. Results and discussion

3.1. Single crystal structure determination

The crystal was mounted on glass fibers. X-ray data were collected using a Bruker AXS SMART APEX diffractometer with Mo–K_α radiation at 100 K using the SMART suite of Programs. Data were processed and corrected for Lorentz and polarization effects using SAINT and for absorption effect using SADABS. Structural solution and refinement were carried out using the SHELXTL suite of programs. The structure was solved by direct methods to locate the heavy atoms followed by difference maps for the light, non-hydrogen atoms. The details of the crystal data and refinement are given in Table 1. The molecular structure with thermal ellipsoids at 50% probability is represented in Fig. 3. The molecular packing with intermolecular hydrogen bonding is shown in Fig. 4. Crystal packing consists of molecules arranged in head-to-tail fashion. Unit cell consists of 8 molecules and two molecular stacks with each stack having 4 molecules. Molecules in one stack are antiparallel to the molecules of other stack. Along the chain, adjacent molecules are faced in opposite direction. Packing is stabilized by the intermolecular C–H…H and C–H…C bonding. Molecules are stacked along the *c*-axis perpendicular to *ab* plane. The dihedral angle between the two aromatic rings in the molecule is 50.03°. This shows that the deviation is large and the two benzene rings are out of plane.

Table 1
Crystal data and structure refinement table.

Empirical formula	$C_{16}H_{13}BrOS$
Formula weight	333.23
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	$a=13.9411(15)$ Å $b=5.8020(6)$ Å $c=33.496(4)$ Å
Volume	2709.4(5) Å^3
Z	8
Density (calculated)	1.634 mg/m^3
Absorption coefficient	3.176
F(0 0 0)	1344
Crystal size	$0.42 \times 0.20 \times 0.10$ mm^3
Theta range for data collection	1.90–27.48°
Index ranges	$-18<=h<=16$, $-7<=k<=7$, $-39<=l<=43$
Reflections collected	17839
Independent reflections	3104 [R(int)=0.0544]
Refinement method	Full-matrix least-squares on F^2

3.2. Thermal studies

To investigate the thermal stability of the crystal 3Br4MSP, thermo gravimetric analysis was carried out. Powdered sample of the crystal was selected for this purpose and the analysis was carried out under nitrogen atmosphere at a heating rate of 10°/min using Perkin–Elemer simultaneous TGA/DTA analyzer. The results of the analysis are shown in Fig. 5. The DTA curve implies the first endothermic peak at 92.78 °C , which corresponds to the melting point of the crystal. The second broad endothermic peak from 270 to about 400 °C corresponds to the first phase of the TG curve indicating major decomposition of the sample. The exothermic peak of the DTA at 400.89 °C corresponds to the weight loss of the sample due to evaporation.

3.3. Microhardness study

The mechanical studies of chalcone crystals were made by Vickers and Knoop microhardness tests at room temperature. In these methods the selected faces were indented gently by varying the loads for a dwell period of 10 s using both Vicker's and Knoop indenter attached to a research microscope Clemex. For a particular load, at least five well-defined impressions were considered and the average of all the diagonals (d) was considered. The Vickers hardness number (H_v) was calculated using the standard formula $H_v=1.8544\ P/d^2$, where P is the applied load in kg, d in mm and H_v is in kg/mm^2. The average diagonal length (d) was considered for the calculation of the Knoop hardness number (H_k) using the relation, $H_k=14.229\ P/d^2$, where P is the applied load in kg, d in mm and H_k is in kg/mm^2. The hardness test was carried out for the loads 3, 5 and 10 g. The cracks started to appear at the load of 10 g and at 25 g load severe cracks were observed around the indenter due to the release of the internal stress locally initiated by indentation. This affected the accurate measurement of indentation length due to large reflecting area surrounding the indented spot. It was observed that both Vickers and Knoop hardness number decreases with increasing