Optics and Laser Technology 93 (2017) 143–148

Contents lists available at ScienceDirect

Optics and Laser Technology

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

Full length article

Growth and characterization of ethyl 4-hydroxybenzoate single crystals by modified vertical Bridgman technique

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ARTICLE INFO

Article history:
Received 15 September 2016
Received in revised form 8 January 2017
Accepted 14 February 2017

Keywords:
Organic compounds
Crystal growth
Bridgman technique
Optical properties
Thermal properties

ABSTRACT

The ethyl 4-hydroxybenzoate single crystals were grown by modified vertical Bridgman technique using two different temperature profiles. The grown ethyl 4-hydroxybenzoate crystals were confirmed by single crystal X-ray diffraction studies. Fourier Transform Infrared spectroscopy (FTIR) studies is used to identify the functional groups of the grown ethyl 4-hydroxybenzoate. The thermal behaviour of the ethyl 4-hydroxybenzoate was analyzed by the thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetric (DSC) analysis. The grown crystals were subjected to UV-Vis-NIR, fluorescence, photoconductivity, Vickers microhardness, dielectric studies and these results were compared.

1. Introduction

In the recent years organic single crystals have been useful in the field of optical signal processing, optical data storage, optical limiting, optical logic gates, lasers, molecular electronic devices, thermoelectric, sensors, detectors, scintillations, colour displays, etc. [1–5]. Good quality single crystals were needed for device fabrication and optical applications. Crystal growers used several crystal growth techniques for growing organic single crystals mainly solution and melt growth techniques. Selection for the growth techniques are mainly depending on the properties of the materials [6]. In the melt growth technique, for increasing the crystalline perfection the researchers used the various types of ampoules [7–13]. The vertical Bridgman technique is an important growth technique, compared to other growth techniques to grow large size organic single crystals with good crystalline perfection. In melt crystal growth, the furnace temperature profile is the pivotal factor for determining the crystalline perfection.

The benzoate family single crystals have excellent nonlinear optical properties such as methyl p-hydroxybenzoate [14], 2-amino 4-picolinium 4-aminobenzoate [15], ethyl p-amino benzoate [16], piperidium p-hydroxybenzoate [17], ethyl p-aminobenzoate [18], 2-amino pyridium 2-chloro 4-nitrobenzoate [19], benzimidazolium p-hydroxybenzoate [20], butyl 4-hydroxybenzoate [21]. The ethyl 4-hydroxybenzoate is a benzoate family material. The ethyl 4-hydroxybenzoate is a non-hygroscopic, non-toxic compound which decomposes above its melting point. It also has a unique para substituted aromatic compound having a combination of 4-hydroxybenzoate and ethanol with two distinct extremities of melting and boiling points, viz., 215 °C, 336 °C and −114 °C and 78 °C respectively [22,23]. The ethyl 4-hydroxybenzoate has an interesting isomer structural molecule of 253 compounds in its molecular formula [24]. The ethyl 4-hydroxybenzoate possesses carbonyl group (C═O), in this group emits fluorescence properties [21]. The ethyl 4-hydroxybenzoate crystal was grown by using the solution growth [25]. In the present study ethyl 4-hydroxybenzoate has been grown by the modified vertical Bridgman technique using two different temperature profiles. The grown crystals were confirmed by single crystal XRD and FTIR studies. The melting, decomposition and crystallization points were analyzed by TG/DTA, DSC studies. The crystals grown on two furnaces with different temperature profiles were analyzed by UV–Vis–NIR, fluorescence, photoconductivity, Vickers microhardness and dielectric studies and their results were discussed and compared.

2. Crystal growth

The ethyl 4-hydroxybenzoate organic single crystals were grown by the modified vertical Bridgman technique using two different temperature profiles. A specially designed nano stepper

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http://dx.doi.org/10.1016/j.optlastec.2017.02.017
0030-3992/

motor drive was used for the translation of the ampoules into the furnaces. The temperature profile of the furnaces was measured and plot the graphs are shown in Fig. 1. It shows that the temperature profile of the furnace 1 has steep decrease of temperature and the furnace 2 has gradual decrease of temperature. The advantage of using the transparent furnaces is that the nucleation can be directly observed. If multi-nucleation occurs during growth the solidification has to be restarted.

In the crystal growth used two single wall ampoules made of borosil glass of length 30.5 cm, cone height 6.5 cm and diameter 1.6 cm. The deionised water and the organic solvent methanol were used to clean the ampoules and they were placed in a hot oven for 24 h at 200 °C to remove moisture. The ethyl 4-hydroxybenzoate of purity 99% was purchased from Sigma–Aldrich (product number: 111988). The material was filled with two ampoules and evacuating it into 10^{-4} torr, using a high vacuum system, then sealed off and placed in two different transparent single zone vertical Bridgman furnaces. It was maintained for 12 h to attain thermal equilibrium position. It is helpful to avoid the bubble formation during the growth. The translations of ampoules begin from the higher region to the lower region. For the crystal growth used translation rate of 9 mm/day. Once the ampoule reached its crystallization point the crystal growth started at the tip of the ampoules and crystal started its growth uniformly from tip to top. After 10 days, the ethyl 4-hydroxybenzoate single crystals were successfully grown. To collect the grown crystals, the temperatures of the furnaces were lowered to a cooling rate of 1 °C/h till it reached the room temperature to avoid cracks on the crystal due to the difference in the thermal expansion coefficient between the ampoule and the crystal. A standard diamond wheel cutter was used to remove crystal from the ampoules. As grown crystal for profile 1, profile 2 and the cut and polished portion of profile 2 grown crystals are shown in Fig. 2(a)–(c).

3. Results and discussions

3.1. Single crystal X-ray diffraction studies

Single crystal X-ray diffraction analysis was carried out to determine the unit cell dimensions of the grown ethyl 4-hydroxybenzoate single crystal. The single crystal X-ray diffraction was recorded by the Enraf Nonius CAD4 Single crystal X-ray diffractometer, it is used to determine the unit cell dimensions. The obtained unit cell dimensions were well agreement with the reported values [25,26]. The grown crystal belongs to monoclinic system with space group $P2_1/c$. The calculated unit cell dimensions of vertical Bridgman grown crystal and the reported values are tabulated in Table 1.

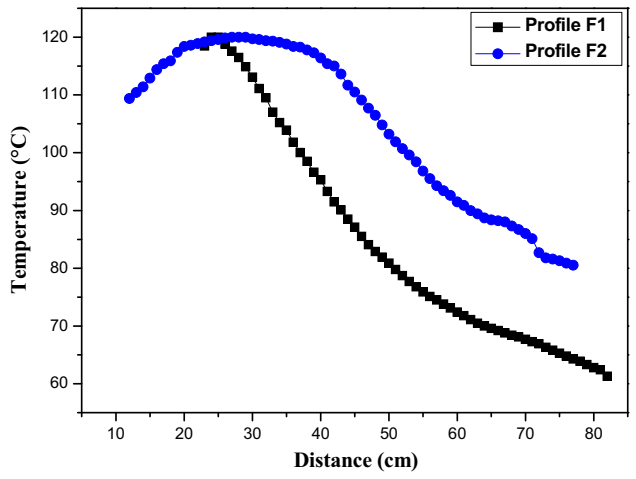

Fig. 1. The temperature profiles of furnaces 1 and 2.

3.2. Fourier Transform Infrared Spectroscopy studies

Fourier Transform Infrared Spectroscopy (FTIR) is an important characterization technique which is used to studies the different functional groups of the grown ethyl 4-hydroxybenzoate. FTIR spectrum of the range 4000–400 cm^{-1} was measured using Perkin Elmer spectrometer by the KBr pellet technique. The ethyl 4-hydroxybenzoate FTIR spectrum is shown in Fig. 3. It was noted that the peak obtained at 3201.77 cm^{-1} was due to O—H stretching vibration. The peak observed at 2976.19 cm^{-1} is due to aliphatic CH_2 stretching vibrations. The peak observed at 1595.75 cm^{-1} is due to C=C stretching. The C—H deformation occurred at 1448.17 cm^{-1}. The ester —COO— group of C=O strong stretching vibration appeared at 1674.51 cm^{-1}. The peaks observed at 1157.57 cm^{-1} and 849.01 cm^{-1} were due to aromatic C—H in plane and out of plane bending respectively [27,28].

3.3. Thermal properties

The thermal properties of the ethyl 4-hydroxybenzoate was analyzed by SDT Q600 instrument. The ethyl 4-hydroxybenzoate was taken in a ceramic crucible and analyzes the temperature ranging from 30 to 350 °C in nitrogen atmosphere, at a heating rate of 10 °C per minute. The differential thermal analysis curve shows a sharp endothermic peak observed around 119 °C which is assigned as the melting point of the grown crystal, it is shown in Fig. 4a. In thermogravimetric analysis shows there was no remarkable weight loss before the melting point of the material has been noticed. The thermo gravimetric analysis (TGA) curve shows that the decomposition taking place in a single stage weight loss with corresponding temperature ranging from 140 to 227 °C, it may be releases the gaseous by-products. The differential thermal analysis shows that the endothermic peak observed near 227 °C was assigned as the decomposition of the grown ethyl 4-hydroxybenzoate. The Q20 V24.2 Build 107 module Differential Scanning Calorimetry was used to analyze the melting and crystallization points of the material and it is shown in Fig. 4b. The DSC heating and cooling curves were used to identify the melting point and crystallization point of the material respectively and the material has melting point around 119 °C and crystallization point around 109 °C. The super cooling temperature has been calculated using the standard formula:

$$\Delta T = T_m - T_c$$
$$\Delta T = 119\,^{\circ}C - 109\,^{\circ}C$$
$$= 10\,^{\circ}C$$

where ΔT is the super cooling temperature, T_m is the melting point and T_c is the crystallization point. The obtained super cooling temperature of the ethyl 4-hydroxybenzoate is 10 °C.

3.4. Optical properties

The optical properties of the grown ethyl 4-hydroxybenzoate single crystals were analyzed by Perkin-Elmer Lambda-35 spectrophotometer. It is used to record the transmission spectrum ranging from 190 to 1100 nm. The crystals of the same thickness 1.5 mm were used for the characterization studies. The optical transmittance of the grown ethyl 4-hydroxybenzoate crystals in profile 1 and 2 were 55% and 65 % respectively and the cut off wavelength were around 306 nm, it is shown in Fig. 5a. The crystal grown in profile 2 was higher transmission than that of profile 1