Physica B 427 (2013) 91–96

Contents lists available at SciVerse ScienceDirect

Physica B

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

Growth and characterization of third order nonlinear optical material: Isatin

B. Thirumalaiselvam [a,b,*], R. Kanagadurai [a], D. Jayaraman [a], V Natarajan [c]

[a] Department of Physics, Presidency College, Chennai 600005, India
[b] Departmen of Physics, P.B. College of Engineering, Chennai, India
[c] Department of Physics, Rajalakshmi Institute of Technology, Chennai, India

ARTICLE INFO

Article history:
Received 28 April 2013
Received in revised form
25 June 2013
Accepted 26 June 2013
Available online 3 July 2013

Keywords:
Solution growth method
Single crystal XRD
UV–vis–NIR absorption
FTIR spectrum
Z-scan technique
Third order non-linear property

ABSTRACT

Isatin, an indole derivative, is a bioactive and nonlinear active material with broad range of applications in synthetic, biological and clinical activity and optoelectronics and photonics. Isatin single crystals were grown by the solution growth method. The grown crystals were characterized by single crystal XRD, UV–vis–NIR, FTIR spectral analysis, dielectric and thermal studies. Kurtz and Perry powder technique reveals the absence of second harmonic generation. The estimations of third order non-linear optical properties like non-linear absorption co-efficient (β), non-linear refractive index (n_2) and susceptibility [$\chi^{(3)}$] using Z-scan technique confirm the third order NLO behaviour of the material and these results indicate that the crystal exhibits saturation absorption and self-focusing performance.

1. Introduction

The search for new frequency conversion material has led to the discovery of many semi-organic materials which have large non-linearity, high resistance to laser induced damage, low angular sensitivity, and good mechanical hardness. Indole is a powerful pharmacodynamic material and it has been reported to possess a wide variety of important biological properties such as anti-inflammatory, antibacterial, anticonvulsant and antioxidant [1–3]. Among the indoles, isatin (indole-2,3-dione), a yellow to red crystalline solid material and a versatile heterocyclic aromatic compound with diketones at 2 and 3 positions, present in mammalian tissues and body fluids [4,5], is probably one of the most important derivatives. Isatin crystals belong to centrosymmetric group with chemical formula $C_8H_5NO_2$. Isatin crystals play an important role in the manufacturing of organic light-emitting devices (OLEDs), with the emission of red colour of reasonable external quantum efficiency and power efficiency [6]. Besides bioactivities, isatin exhibits third order nonlinear optical (NLO) property and finds applications in optical communication and in the fabrications of optical information storage, optical limiting and switching devices. For device fabrications, the material should be available in crystalline form. In this work, we report the growth and characterization of isatin single crystals. Single crystals of isatin were grown successfully for the first time using the solution growth technique. The grown crystal was then subjected to single crystal XRD, UV–vis–NIR and FTIR spectral analysis, dielectric and thermal studies to analyze the crystal system, transmission range of the crystal, the functional groups present in the material, dielectric and thermal behaviours respectively. The second order nonlinearity of Isatin was found to be absent when tested by the Kurtz–Perry technique. The Z-scan technique, a popular method for studying the third order optical non-linearity of the material, has the advantages of high sensitivity and simplicity [7]. By this technique one can simultaneously measure the magnitude and sign of the non-linear refraction and non-linear absorption, which are associated with the real part $\chi_R^{(3)}$ and imaginary part $\chi_I^{(3)}$ of the third order susceptibility. The Z-scan technique has been employed to measure the third order non-linear optical properties of semiconductors, dielectrics, organic and carbon based materials and liquid crystals [8–11]. Third order NLO material is a potential material which can be used in optical switching and optical limiting devices [12,13].

2. Experimental procedure

2.1. Growth of isatin

In order to grow the single crystals of isatin, a saturated solution of isatin was prepared at room temperature (30 °C) using methanol as solvent. The solution was covered with tissue paper and pricked with pin to make suitable number of holes for slow and steady evaporation

* Correspondence to: Department of Physics, P.B. College of Engineering, Irungattukottai, Sriperumbadur, Kanchipuram District, Tamilnadu, India.
Tel.: +91 9965096534.
E-mail address: bthirumalaiselvam@gmail.com (B. Thirumalaiselvam).

0921-4526/$ - see front matter Crown Copyright © 2013 Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.physb.2013.06.035

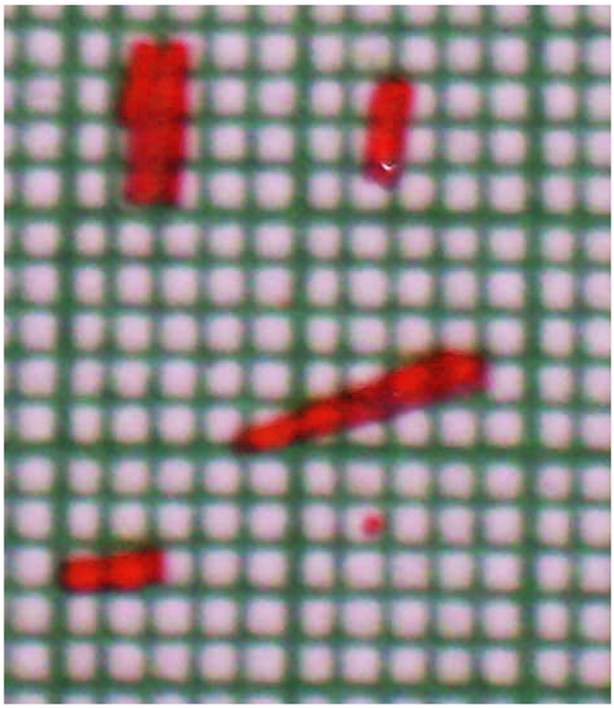

Fig. 1. Photograph of as-grown crystal of Isatin.

of the solution. The solution was then placed in a constant temperature bath to maintain the solution at constant temperature (30 °C). When the solution evaporates, the saturation gradually attains supersaturated level leading to nucleation and the growth of the crystals. The size and purity of crystal were improved by repeated crystallization process. After 2 weeks, transparent single crystals of size $5 \times 1.37 \times 1\ mm^3$ were harvested. The as-grown Isatin crystals are shown in Fig. 1.

2.2. Characterization studies

Single crystal XRD data of isatin were obtained using an automatic X-ray diffractometer (MESSERS ENRAF NONIUS,CAD-4, Netherlands) with a Cu Kα radiation ($\lambda = 1.5406$ Å). Powder XRD data of isatin were collected using a Rich seifert diffractometer. The absorption spectrum of isatin crystal was recorded in the wavelength region of 300–2000 nm using VARIAN CARY 5E model spectrometer. FTIR spectra of Isatin were obtained in the range of 450–4000 cm^{-1} using IFS 66 V, FTIR spectrometer. Dielectric studies were carried out at different temperatures using HIOKI 3532 LCR HITESTER in the frequency range from 50 Hz to 5 MHz. Thermal behaviour of the material was analyzed using NETZSCH-Geratabau thermal analyzer. The technique developed by Kurtz and Perry was used to test the presence of second order nonlinearity of the material. The Z-scan technique was employed for analyzing the third order non-linear optical behaviour of the material.

3. Results and discussion

3.1. XRD Studies

Single crystal X-ray diffraction analysis of isatin material was carried out using Enraf Nonius CAD-4 X-ray diffractometer. The lattice parameters estimated from the analysis are $a = 7.175$ Å, $b = 14.676$ Å and $c = 6.232$ Å and $\alpha = \beta = 90^\circ$ and $\gamma = 93.89^\circ$ and $V = 656.2314\ Å^3$. It is observed that Isatin single crystal belongs to monoclinic system and space group $P2_1/b$. The space group suggests that the crystal belongs to centro-symmetric group and the absence of second order nonlinearity in the material.

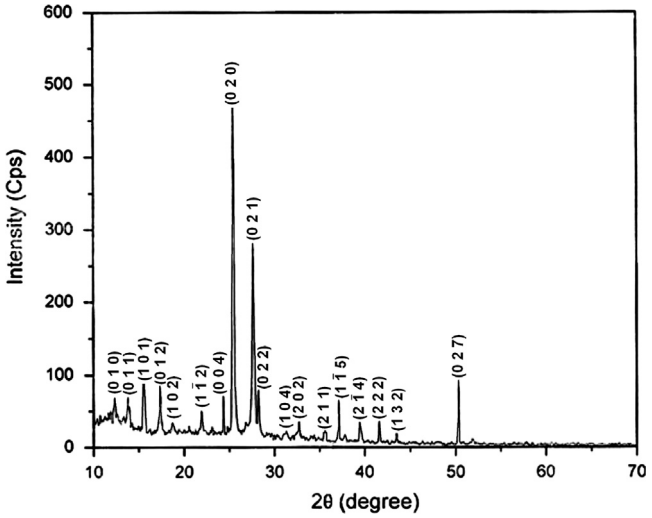

Fig. 2. Powder XRD pattern of isatin.

Table1
Powder XRD data of isatin.

2θ (deg)	d (Å)	Intensity	hkl	Lattice parameters
12.3241	7.1761	68	010	
13.8099	6.4072	65	011	
15.5529	5.6929	110	101	
17.3349	5.1115	85	012	
18.7106	4.7386	34	102	
21.9439	4.0472	51	$1\bar{1}2$	
24.3360	3.6545	73	004	$a = 7.183$ Å
25.4502	3.4970	514	020	$b = 14.775$ Å
27.6568	3.2228	279	021	$c = 6.256$ Å
28.2275	3.1589	78	022	$\alpha = \beta = 90^\circ$
31.2855	2.8567	22	104	$\gamma = 93.78^\circ$
32.7049	2.7359	35	202	Volume (V) = 663.9419 $Å^3$
35.5766	2.5214	23	211	
37.1296	2.4194	66	$1\bar{1}5$	
39.4808	2.2806	34	$2\bar{1}4$	
41.5959	2.1694	37	222	
43.4739	2.0799	20	132	
50.3175	1.8119	93	027	

A finely crushed powder of isatin was subjected to powder X-ray diffraction analysis using a rich seifert diffractometer with CuKα ($\lambda = 1.540598$ Å) radiation. The sample was scanned over the range of 10–70° at a scan rate of 1°/min. The recorded powder X-ray spectrum is shown in Fig. 2 and the peaks have been indexed. Using the data obtained from powder XRD spectrum, the lattice parameters were calculated and presented in Table 1. The results of single crystal XRD and powder XRD studies are found to be in good agreement with the reported values [14].

3.2. UV–vis–NIR study

For optical device fabrication, the crystal should be highly transparent over a considerable region of wavelength [15]. The recorded optical absorption spectrum of the crystal is shown in Fig. 3. From the spectrum, it is noticed that the absorption of the crystal is considerably low in the wavelength region of 300–1200 nm. The prominent peaks observed in the spectrum may be due to overtones or the combination bands of either stretching or bending vibrations in the middle infrared region.