Available online at www.elixirpublishers.com (Elixir International Journal)

Materials Science

Elixir Materials Sci. 73 (2014) 26102-26104

ISSN: 2229-712X

Optical and mechanical studies on unidirectional grown Tri-nitrophenol p-hydroxyacetophenone single crystal

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ARTICLE INFO

Article history:
Received: 28 June 2014;
Received in revised form: 20 July 2014;
Accepted: 2 August 2014;

Keywords
Crystal growth, X-ray diffraction, Optical materials and properties, Mechanical properties.

ABSTRACT

The tri-nitrophenol p-hydroxyacetophenone (TNPHAP) single crystal was grown from aqueous solution by Sankaranarayanan-Ramasamy (SR) unidirectional growth method. The grown crystal with cylindrical shape about 12 mm diameter and 55 mm length was obtained by S-R technique. The formation of TNPHAP was confirmed by single crystal and powder X-ray diffraction studies. The optical properties of grown crystal has been analyzed by UV-Vis absorption studies. The mechanical strength of the grown crystal has been studied using Vicker's microhardness tester. The dielectric constant and dielectric loss was studied as the function of frequencies. The results are discussed in detail.

Introduction

Nonlinear optics (NLO) is the precursor of current research, because of its importance providing the key functions of frequency shifting, optical modulation and optical memory for the emerging techniques in areas such as telecommunications and optical interconnections [1,2]. The design and synthesis of organic molecules exhibiting NLO properties have been motivated by the tremendous potential for their applications in the fast developing domains of optoelectronics and photonic technologies. An organic molecule should possess large second-order hyperpolarizability to exhibit good non-linear optical properties [3-5]. The materials with non-centro symmetric structure possess nonlinear properties in the even-order susceptibilities. In a centrosymmetric structure, however, the even-order nonlinear susceptibilities are zero in the electric dipole approximation [6-8]. Tri-nitrophenol p-hydroxyacetophenone (TNPHAP), which crystallizes in the monoclinic system with space group $P2_1/c$, and possess nonlinearity in the third harmonic generation (THG). The nonlinear optical property is measured using the Z-scan technique [9]. The unidirectional Sankaranarayanan-Ramasamy [10,11] solution growth method attracted the researchers due to the growth of defect-free transparent bulk single crystals along a particular axis. Simple experimental techniques, maximum solute-solid conversion and prevention of the microbial growth are the interesting features of this technique. In the present work, we report for bulk single crystal of the TNPHAP grown from the unidirectional method. The grown crystals were subjected to single crystal and powder X-ray diffraction (XRD) analysis, UV-Vis-NIR spectral analysis, Vickers hardness test, dielectric studies.

Experimental procedure

Growth of tri-nitrophenol p-hydroxyacetophenone single crystal

The slow evaporation technique was used for crystal growth. The p-hydroxyacetophenone (99.99%) and picric acid (99.9%) were taken in a 1:1 molar ratio. This has been further purified by repeated recrystallization process to improve the optical quality. The saturated solution of tri-nitrophenol p-hydroxyacetophene was obtained by dissolving the re-crystallized salt in methanol with continuous stirring using a magnetic stirrer. The prepared solution was maintained at 37°C in constant temprature bath. Good quality seed crystals with perfect external morphology were obtained within a period of 3 days.

Experimental Setup and Crystal Growth

An optically cleared seed crystal was mounted on the bottom of the ampule, filled with supersaturated solution of TNPHAP and placed along the axis of the growth assembly. Here, an assembly of alternating ring heater serve as a temperature gradient for the growth as shown in Figure 1. The temperature at the top of the ampule was maintained at 37°C using a temperature controller setup for the evaporation of the saturated solution. The temperature gradient makes the concentration gradient maximum at the bottom and minimum at the top of the ampule for avoiding the spurious nucleation along the axis of the ampule. The growth rate of the crystal was found to be 3 mm per day. Crystal of 55 mm length has been grown successfully within a period of 19 days, the photograph of the grown crystal is shown in figure 2.

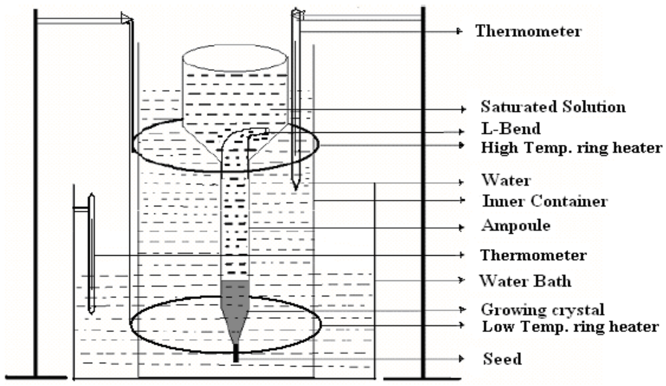

Figure 1. Crystal growth setup

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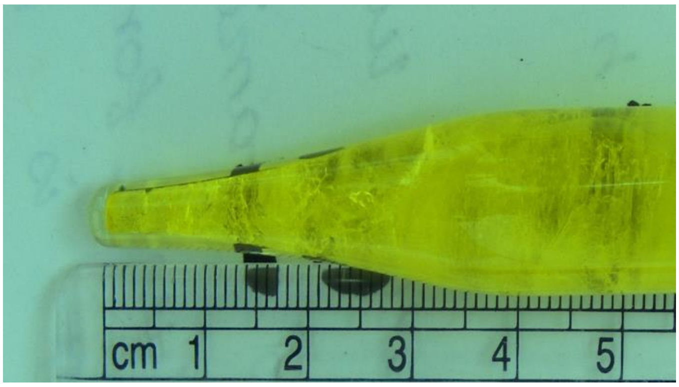

Figure 2. Photograph of unidirectional grown single crystal

Results and discussion

Single crystal X-ray diffraction studies

Single crystal X-ray diffraction (XRD) analysis for the grown tri-nitrophenol p-hydroxyacetophenone crystal has been carried out to confirm the crystalline and also to identify the unit cell parameters using a Bruker Kappa APEX-2 diffractometer with MoKα (λ=0.71073Å) radiation. The crystal system is monoclinic and space group $P2_1/c$ unit cell dimensions of a=8.152(5) Å b=26.345(5) Å c=8.147(5) Å and is well matched with the reported literature [7].

Powder XRD analysis

The powdered sample of the grown crystal was also subjected to powder X-ray diffraction analysis using Rich Seifert X-ray diffractrometer employing CuKα radiation (λ = 1.5418 Å). The peaks observed in the X-ray diffraction spectrum were analyzed and the lattice parameters were calculated by the least square fit method. The data obtained by the powder X-ray diffraction analysis in accordance with the single crystal X-ray diffraction data. It is clear that for the crystal $a \neq b \neq c$, $\alpha = \gamma = 90°$ and $\beta \neq 90°$, which ensures that the grown TNPHAP crystal is of monoclinic structure. The powder X-ray diffraction pattern is shown in Figure 3.

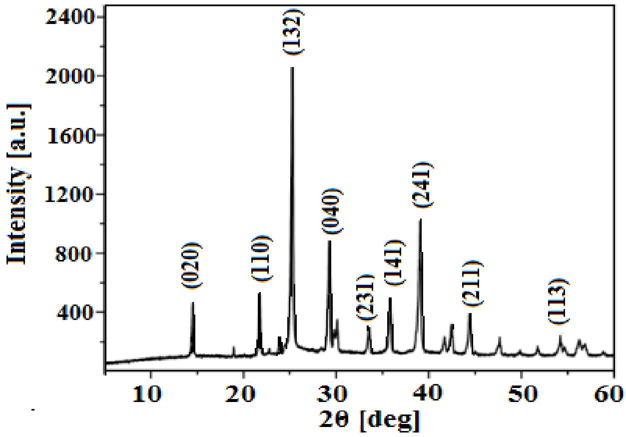

Figure 3. Powder XRD pattern of TNPHAP single crystal

Optical absorption spectrum

The optical absorption spectral analysis for the grown crystal was carried out between 200 and 2000 nm using VARIAN CARY 5E spectrophotometer and is shown in Figure 4. The resultant spectrum shows that the crystal has very low absorbance in the entire visible and IR region. The UV cut-off wavelength for the grown crystal is found to be at 320 nm. Hence TNPHAP crystal can be used for optoelectronic applications.

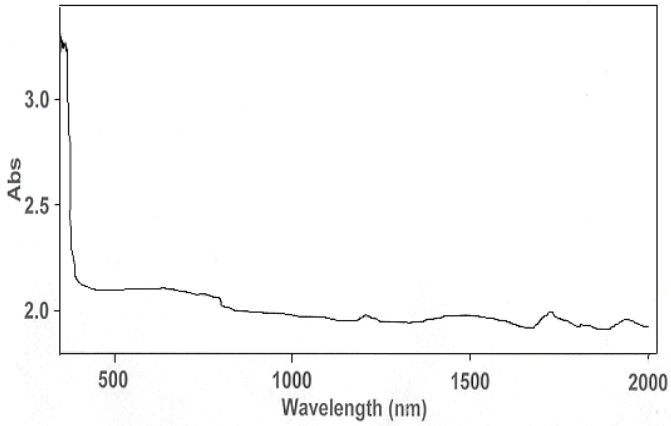

Figure 4. UV spectrum of grown TNPHAP single crystal

Micro hardness studies

Hardness is the resistance offered by a material to the localized deformations caused by scratching or indentations [13]. The indentation hardness is measured as the ratio of applied load to the surface area of the indentation. Microhardness measurement was made on the well-defined plane of the grown crystal using Vickers microhardness tester fitted with a pyramidal indenter. The grown crystal with smooth and dominant faces was selected for microhardness studies. Indentations were made for varying load and the average value of diagonal length was used to calculate the microhardness. Vickers microhardness number as calculated using the relation,

$$Hv = 1.8544 \frac{p}{d^2} kg/mm^2 \qquad (1)$$

where P is the applied load in kg and d is the mean diagonal length of the indenter impression in millimeter. The as-grown crystal exhibits the reverse indentation size effect (RISE) in which the hardness value increases (Figure 5) with increase in load [14]. The hardness value found to be is 65.2 kg/mm^2 that the grown crystal belongs to softer material category which is systematically higher than other known organic NLO materials [15, 16].

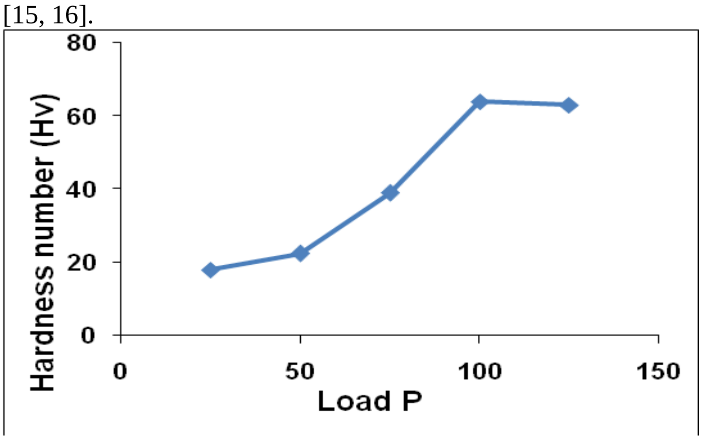

Figure 5. Plot of P vs Hv for TNPHAP crystal

Dielectric Studies

Dielectric constant and dielectric loss measurements were performed on unidirectional grown TNPHAP single crystals using a Hioki Hitester model 3532-50 LCR meter and conventional two terminal sample holders. The techniques used for the measurement of dielectric constant are either reflection coefficients or resonant frequencies. In the later case, material is characterized to load a resonant cavity and the sample permittivity is evaluated from the shift of the resonant frequency value, compared to that of the empty (unload) cavity. The dielectric constant and dielectric loss have been calculated using the equations (2) and (3).

$$\varepsilon = \frac{cd}{A\varepsilon_0} \quad (2)$$

$$\varepsilon' = \varepsilon \tan\delta \quad (3)$$

Where d is the thickness of the sample, A is the area of the sample. Dielectric measurements of grown crystal are shown in Figure 6, Figure 7. From the spectrum, it is observed that the dielectric constant and dielectric loss decreases slowly with increasing frequency and attains saturation at higher frequencies. The high dielectric constant value of the crystal at low frequency is attributed due to space charge polarization [17, 18]. In accordance with Miller rule, the lower value of dielectric constant at higher frequencies is a suitable parameter for the enhancement of optical applications [19]. The characteristic of low dielectric loss with high frequency for the sample suggests that the crystal possess enhanced optical quality with lesser defects and this parameter play a vital role for the construction of devices from nonlinear optical materials [20].

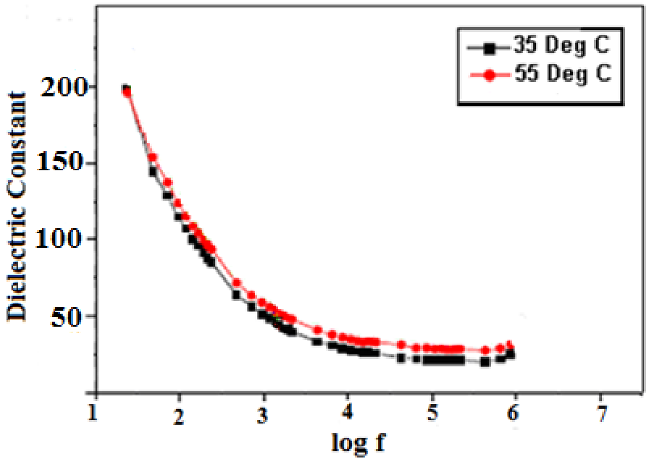

Figure 6. Plot of Dielectric constant vs log f

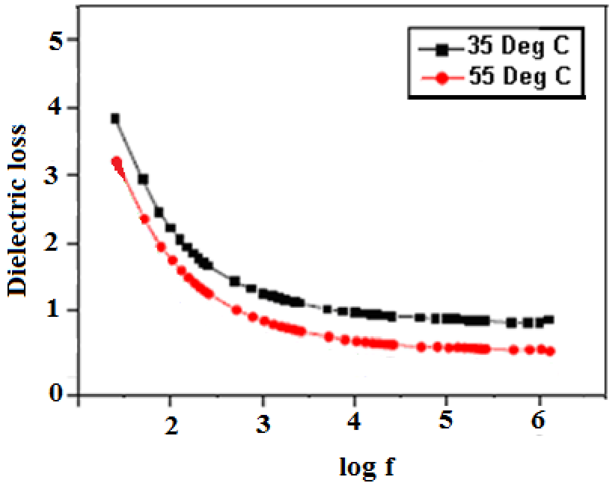

Figure 7. Plot of Dielectric loss vs log f

Conclusions

The organic nonlinear optical bulk single crystal of tri-nitrophenol p-hydroxyacetophenone was grown by unidirectional growth technique. Single crystal X-ray diffraction and powder diffraction studies of the crystal reveal that the material belongs to monoclinic system and space group $P2_1/c$ with unit cell parameters a=8.152(5) Å b=26.345(5) Å c=8.147(5) Å. The grown crystal has good transparency range in the entire visible and near IR region with UV cutoff wavelength at 320 nm. Mechanical hardness studies reveal that Vicker's hardness number increases as the load increases and then decreases for higher loads. The dielectric studies revealed that TNPHAP has low dielectric loss with less power dissipation and hence this crystal can be used for optical applications. With these promising physicochemical properties, tri-nitrophenol p-hydroxyacetophenone single crystal can be used as a potential material for nonlinear optical applications.

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