Growth and Characterization Studies of Triphenyl Methane Single NLO Crystals

X. Martina Mejeba, Prem Anand Devarajan*
Material Research Centre, Department of Physics,
St. Xavier's College (Autonomous),
Palayamkottai, Tamilnadu, India

***Abstract*— In this paper, we report the synthesis, growth and characterization of an organic NLO single crystal Triphenyl methane. The title compound was synthesized and single crystals was grown employing the slow evaporation technique at constant temperature. The grown single crystal was characterized by single crystal XRD; powder XRD, FTIR, , UV-Vis, and microhardness studies. From the XRD study, it is found that the crystals belong to orthorhombic system with a space group $P2_12_12_1$. The FTIR spectrum was recorded to identify the various functional groups present in the compound. The optical transparency was determined by UV-visible spectroscopy. The second harmonic generation (SHG) efficiency of the crystal was obtained using ND-YAG laser which is found to be 1.9 times that of KDP.**

Keywords--- Crystal growth, slow evaporation technique,Triphenyl methane, FTIR ,UV, microhardness, photoconductivity, nonlinear optical material

I. INTRODUCTION

NLO properties of large organic molecules and polymers have been the subject of extensive theoretical and experimental investigations during the past two decades and they have been investigated widely due to their high nonlinear optical properties, rapid response in electro-optic effect and large second or third order high polarizabilities compared to inorganic NLO materials. Organic crystals have shown to have potential applications in nonlinear optics. Nonlinear optics (NLO) is at the forefront of current research because of its importance to provide the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging techniques in areas such as telecommunications, signal processing, and optical interconnections [1 - 3]. Organic materials have been of particular interest because the nonlinear optical response in this broad class of materials is microscopic in origin, offering an opportunity to use theoretical modeling coupled with synthetic flexibility to design and produce novel materials [4 - 6]. Organic NLO materials have a very large nonlinear susceptibility, which are in many cases several orders of magnitude higher than that of inorganic crystal such as potassium dihydrogen phosphate (KDP) [7 - 8]. Hence in the recent years synthesizing organic crystals have gained high importance [9 - 15]. Dielectric studies have been carried out on Nicotinium Triflouro Acetate single crystal by P.V.Dhanraj et al [16]. Michrohardness studies have been carried out on Glycinium Oxatale single crystals by Satheesh Chandra et al [17]. Growth and thermal studies on doped and pure single crystals of L-Arginium Dinitrate have been carried out by Preema et al [18]. Selvakumar et al have carried out spectral and optical charaterization on Barium Bis- Paranitrophenolate paranitrophenol Tetrahydrate (BBPT) NLO single crystal [19]. Growth and characterization of a new organic nonlinear optical crystal: 1-(3-Nitrophenyl)-5-phenylpenta-2,4-dien-1-one have been carried out by Paratatgouda S Patel et al [20]. Jegatheesan et al have synthesized and carried out characterization on Glycine Trifluoro Acetate single crystal [21]. Crystallization and characterization of NLO active Glycine Copper sulphate crystal have been carried out by Nalini Jeyanthi et al [22].

The title compound Triphenyl methane is a well known chemical reagent. TPM single crystals were grown from the supersaturated solution of Triphenyl methane in Toluene by slow evaporation technique and the results from the characterization studies are reported.

II. GROWTH OF TPM CRYSTALS

6.1 g of Pure Triphenyl methane (99% - Sigma Aldrich) was dissolved in 25 ml of Toluene until a supersaturation was achieved. The supersaturated solution was stirred well for 6 hours at room temperature using a temperature controlled magnetic stirrer to yield a homogenous mixture of solution. Then the solution was filtered thrice using a Whatmann filter paper and was transferred in a beaker covered with airtight thick filter paper so that the rate of evaporation can be minimized. Optically transparent crystals were formed due to spontaneous nucleation. Among them defect free crystals were selected as seeds in order to grow bulk crystals. The synthesized salt was purified by successive recrystallization process. After a period of 12 days single crystals of TPM having dimensions 9x6x2 mm^3 were harvested by slow evaporation method at room temperature. The photograph of the as grown crystal is as shown in Fig. 1

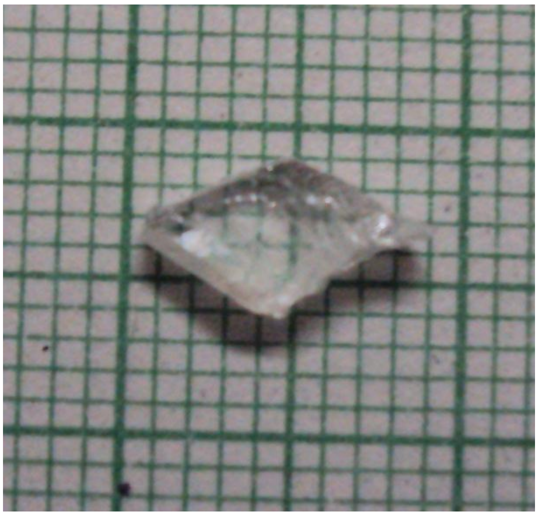

Fig. 1 Photograph of grown single TPM NLO single crystal

III. CHARACTERIZATION STUDIES OF TPM CRYSTALS

A. Single XRD analysis

The single crystal X-ray diffraction was recorded with the Bruker Smart Apex instrument and the wavelength of X-ray used was 0.7093 A° (Target-molybdenum). From single crystal XRD the lattice parameters were calculated and this crystal belongs to orthorhombic. The space group was found to be $P2_12_12_1$. The lattice parameters calculated from single crystal XRD are a = 7.52 A°, b = 14.80 A°, c = 25.58 A° and α= 90.00(0)°, β= 90.00°, γ= 90.00(0)°. The cell volume of the crystal was found to be V = 2847 Â^3.

B. Powder XRD analysis

PXRD studies were carried out to confirm the crystallinity of the sample using XPERT-PRO X-ray diffractometer with the CuKα radiation in the range of 10°-80°, insteps of 10°. The powder XRD pattern is shown in Fig. 2. It reflects the good crystallinity of the grown crystal. The lattice parameters were calculated using TREOR programme which coincides with single crystal XRD results.

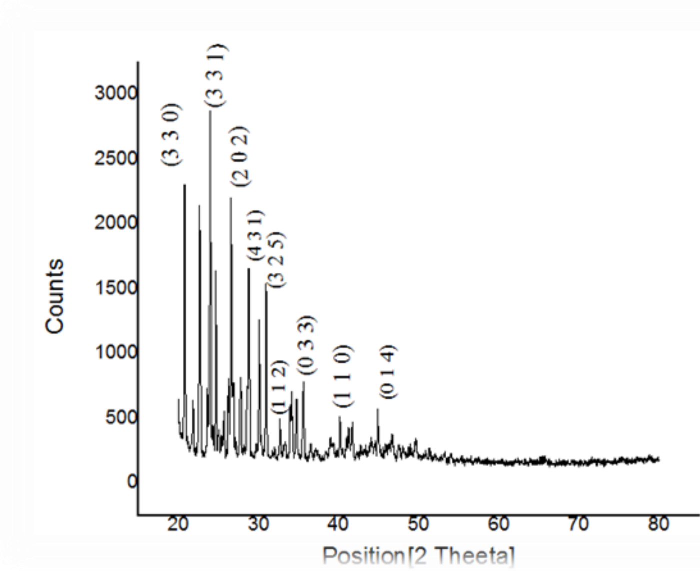

Fig. 2 PXRD analysis of TPM NLO single crystal

Pos. [°2Th.]	d-spacing [Å]	h k l
20.7274	4.28546	0 3 3
21.7645	4.08354	0 1 6
22.6060	3.93341	1 3 2
22.7829	3.90326	0 3 4
23.5611	3.77607	2 0 0
23.9240	3.71962	2 0 1
24.2580	3.66915	1 2 5
24.6408	3.61300	2 0 2
25.0278	3.55800	2 1 1
25.3256	3.51684	2 1 2
25.6886	3.46797	1 3 4
26.2436	3.39588	0 4 3
26.5267	3.36027	2 2 0
26.8261	3.32344	2 2 1
27.1194	3.28817	1 4 1
27.7213	3.21812	0 3 6
28.4909	3.13292	2 1 4
28.7431	3.10343	2 2 3
28.8287	3.09697	1 4 3
30.0384	2.97496	2 3 1
30.8678	2.89688	2 3 2
32.6640	2.74157	1 5 0
33.3272	2.68852	1 5 2
33.8665	2.64693	0 2 9
34.1249	2.62747	2 2 6
34.7221	2.58364	2 4 2
35.6082	2.52135	1 3 8
36.4588	2.46445	3 1 0
38.3703	2.34597	2 4 5
38.9111	2.31460	2 5 1
40.1257	2.24730	3 0 5
40.9783	2.20249	0 2 11
41.2401	2.18911	1 1 11
41.7433	2.16388	2 2 9
42.7301	2.11616	2 5 5
44.0687	2.05494	2 3 9
44.8241	2.02205	1 3 11
46.5840	1.94968	0 6 8
47.4763	1.91510	3 4 5
49.5948	1.83814	1 2 13
51.3400	1.77968	4 2 3
53.1288	1.72391	1 2 14
65.6775	1.42167	3 5 12

Table 1 PXRD data of TPM NLO single crystal

C. FTIR Analysis

In order to analyze the presence of functional groups qualitatively in the grown crystal, the FTIR spectrum was recorded between 400 cm^{-1}and 4000 cm^{-1} using IFS BRUKER 66V spectrometer by KBr pellet technique and the resultant spectrum is shown in Fig. 2. The broad band at 3440.09 cm^{-1}is due to hydrogen bonded O–H stretching indicating the presence of the phenyl group .The alkane stretching of H–C–H is found to be near 3089.60 cm^{-1} and 2934.31 cm^{-1}. The peak at 1670.10 cm^{-1} indicates the presence of C–C=C symmetric stretching and The peak at 1436.79 cm^{-1} indicates the presence of C–C=C asymmetric stretching. The group assignments confirm the chemical structure of Triphenyl methane [23].

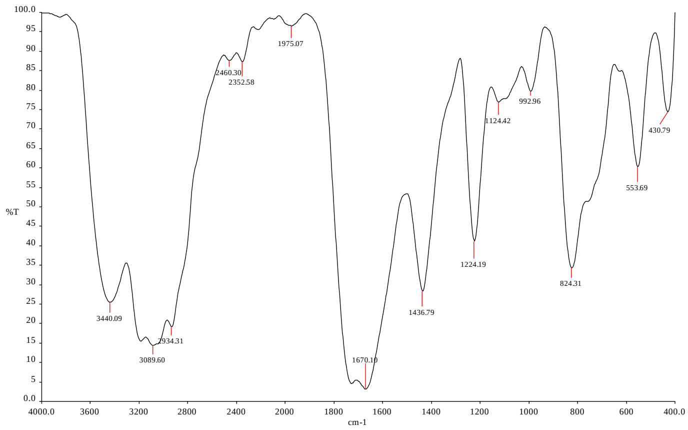

Fig. 3 FTIR Analysis of TPM NLO single crystal

D. UV-vis-NIR analysis

To analyze the optical properties of grown TPM crystal, UV-Vis absorption was recorded. For this, polished sample of 1 mm thick from the grown crystal was used. The recorded UV-Vis-NIR spectrum of TPM is shown in Figure 4. The absorption spectrum of TPM was recorded in the wavelength range between 190 nm and 1100 nm, using Lamda 35 UV-VIS spectrophotometer (Fig. 3) The optical absorption study shows that the UV cut-off wavelength of TPM occurs at 238nm. It is well known that the efficient NLO crystal has an optical transparency at lower cut-off wavelength between 200 and 400 nm [24]. There is no significant absorption in the entire visible region which reveals that it can find applications in the optoelectronic devices. The crystal has good optical transmission in the visible region. The transparency in the visible region for this crystal suggests its suitability for second harmonic generation.

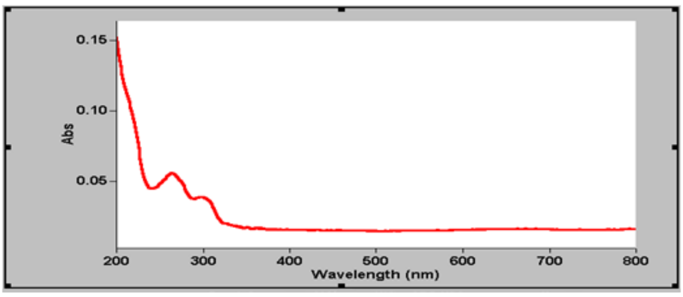

Fig. 4 UV-spectrum of TPM NLO single crystal

E. Microhardness test

Hardness is one of the important mechanical properties to determine the plastic nature and strength of a material. The TPM crystal was placed on the platform of the Vicker's microhardness tester and the loads of different magnitudes were applied over a fixed interval of time. The hardness number was calculated using the relation $H_v = 1.8544(P/d^2)$ kg/mm^2, where P is the applied load in kg and d is the diagonal length of the indentation impression in micrometer. The relation between hardness number (H_v) and load (P) for TPM is shown in Figure 5. The hardness increases gradually with the increase in load. The slope of the line obtained from graph predicts that the value of n is greater than 2. H_v should increase with the increase of P if (n>2) and decrease if (n<2) [25]. Thus, the value satisfies the observed result.

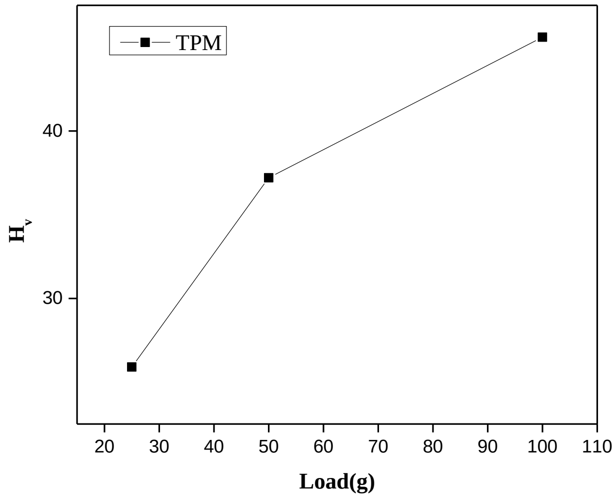

Fig. 5 Microhardness of TPM NLO single crystal

F. NLO studies

The nonlinear optical property of the grown single crystal is tested by passing the output of Nd:YAG Quanta ray laser through the crystalline powder sample. A Q-switched, mode-locked Nd:YAG laser was used to generate about 10.8 mJ/pulse at the 1064 nm fundamental radiation. The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of diameter 0.154 nm. The photodiode detector and oscilloscope assembly measure the light emitted by the sample. Microcrystalline powder of KDP is taken at one end for comparison. Thus the figure of merit of SHG of the sample is estimated. The nonlinear property in TPM was studied using a Q-switched Nd: YAG laser by employing Kurtz powder test [26 - 27]. The fundamental beam of an Nd: YAG laser with 1064 nm wavelength, pulse duration of 35 ns and 10 Hz repetition rate is focused on to the powdered sample. The Second Harmonic Generation (SHG) signal at 532 nm is recorded at various (kg/mm2)points on the sample using a photomultiplier tube. The SHG efficiency is found to be 1.9 times greater than that of inorganic sample of Potassium dihydrogen phosphate KDP.

G. Photoconductivity studies

Photoconductivity provides useful and valuable information about physical properties of materials and offers applications on photo detection and radiation measurements. When photons of energy greater than that of the band gap of the material are incident upon a photoconductive material, electrons and holes are created in the conduction and valence bands, respectively increasing the conductivity of the sample. Photoconductivity property of the grown TPM crystal was measured in the range of 0–2800 V/cm^{-1} using a Keithley picoammeter. The corresponding photocurrent was measured with respect to the applied voltage. The variations of photocurrent (I_p) and dark current (I_d) with applied field were shown in Figure 7. It was observed that both dark current and photocurrent of the crystals increase linearly with the applied electric field but if the dark current is less than the photocurrent, photoconductivity of the TPM crystal is positive

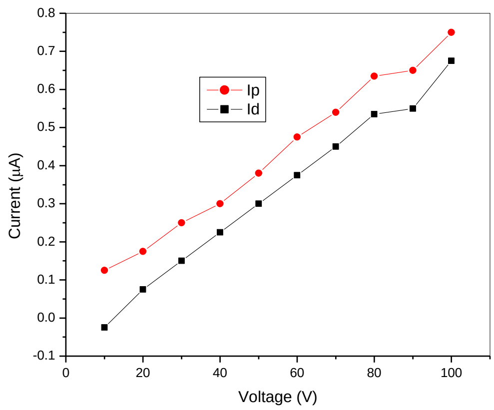

Fig. 6 Photoconductivity of TPM NLO single crystal

III. CONCLUSION

Single crystals of Triphenyl methane was grown using toluene as a solvent at room temperature by slow evaporation method. The grown single crystals was characterized by single crystal XRD and it is confirmed that the crystal belongs to the orthorhombic system. The functional groups were verified using FTIR analysis. The cut-off wavelength was found to be 328 nm^{-1}. The mechanical strength of the grown crystal was found from Vicker's microhardness measurement. The second harmonic generation efficiency by Kurtz-Perry powder technique reveals that the crystal was 1.9 times that of KDP. The photocurrent was greater than the dark current signifying positive photoconducting nature.

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