ISSN: 0974-5823 Vol. 7 No. 4 April, 2022

International Journal of Mechanical Engineering

THIRD HARMONIC GENERATION (THG) STUDIES ON PIPERINE SINGLE CRYSTAL FOR OPTICAL LIMITING APPLICATIONS – A COMPARATIVE ANALYSIS

A. Muthuraja[1], K. Prabavathi[*], S. Kavipriya[*], K. Rubitha[*], S. Pavithra[*], A. Ishwarya[*]

[1]Department of Physics, Theivanai Ammal College for Women (Autonomous), Villupuram, Tamil Nadu. India*

Abstract

Recently more attention has been paid to the growth of organic nonlinear optical single crystals due to their high nonlinear optical efficiency comparable to that of inorganic counterparts. An organic single crystal piperine was grown by slow evaporation solution growth technique (SEST) and vertical Bridgman technique (VBT). Single crystal X-ray diffraction measurements were carried out on both SEST and VBT grown piperine single crystals. The third order nonlinear optical properties like non-linear absorption coefficient (β), non-linear refractive index (n_2) and susceptibility [$\chi^{(3)}$] of crystal were studied using the Z-scan technique. Z- Scan measurements are carried out on SEST and VBT grown piperine single crystals and their results are compared.

Keywords: Single crystal, Microhardness, Bridgman, organic single crystal

1. Introduction

In the last few decades, the search for new nonlinear optical (NLO) materials has been increased because of their potential application in optical modulation, Third harmonic generation (THG) [1], optical signal processing, optical switching [2] and optical data storage devices [3]. The basic structure of the organic NLO materials is based on the π bond system [4]. Due to the overlap of π orbitals, delocalization of electronic charge distribution leads to a high mobility of electron density. The other advantages of organic material over inorganic material are the scope for altering the properties by functional substitutions, high degree of nonlinearity, and high damage resistance [5]. Because of the large nonlinearities and the optical threshold of organic materials, a wide range of such materials have been found by many researchers. Since the growth methods are quite different, the crystals grown by these methods may have different crystalline perfection, which may lead to some differences in their physical properties. In the present communication, we have reported the comparative analysis of the crystals grown by both these techniques by employing. . Piperine is one such non-hygroscopic organic material. The molecular formula is $C_{17}H_{19}NO_3$. Piperine (PPN) single crystals have been successfully grown by slow evaporation solution growth technique (SEST) [6] using methanol as the solvent. From the analysis of the thermal behaviour of piperine, it is observed that there is no decomposition before melting. It is decided to grow these crystals by vertical Bridgman technique (VBT) [7]. Since the growth methods are quite different, the crystals grown by these methods may have different crystalline perfection, which may lead to some differences in their physical properties.

2. Crystal Growth Experimental

2.1 Slow Evaporation Solution Growth Technique (SEST)

Commercially available piperine (98 % purity, molecular weight – 285.3, melting point -138° C) powder was purified by repeated recrystallization process using methanol as the solvent. The recrystallised material was used for the bulk growth of crystals. The solubility was tested in methanol, acetone, water and toluene. It was found that the piperine is highly soluble in methanol. The bulk single crystal was harvested from mother solution after 20 days. Figure 1(b) shows the solution grown piperine single crystals using methanol solvent.

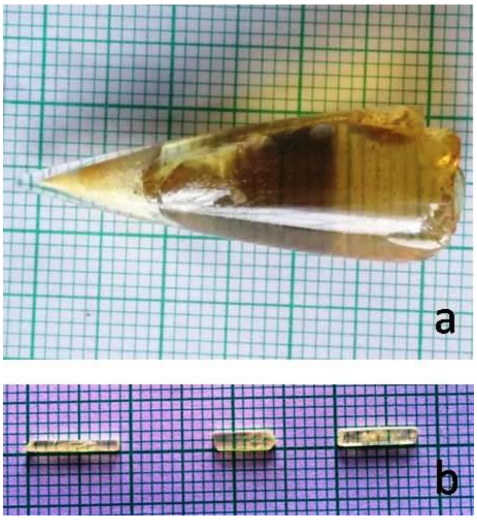


Fig: 1. (a) VBT single Crystal (b) SEST single crystal

2.2 Vertical Bridgman Technique (VBT)

Bulk single crystals of piperine have been successfully grown by the Bridgman technique using a glass ampoule under vacuum. The ampoule with sharp conical tip was preferred for the growth of single crystals of piperine so that the tip acts as a point of initiation for material solidification and also controls the further growth of the crystal. Single wall ampoule was used for the growth. The growth ampoule was well degreased with ethanol and kept in the hot air oven for two days. The two zone resistive heating alumina furnace was used for the growth. The glass ampoule was loaded with piperine powder and evacuated to 10^{-6} torr and then sealed carefully. The ampoule translation speed inside the furnace was 1mm/h. During the post growth, the furnace was cooled to room temperature at the cooling rate of 1°C/h. The grown crystal was detached from the ampoule using diamond wheel cutter. A transparent single crystal was harvested after 15 days. The as grown piperine single crystal inside the ampoule is shown in Figure 1(a).

3. Z-scan measurements

The single beam Z-scan is a well known technique for measuring an absolute magnitude of the nonlinear refraction coefficient of the investigated compound. The Z-scan technique depends on the distortions generated in the spatial and temporal profile of the input beam that passes through the sample. The third order nonlinear refractive index n_2 and nonlinear absorption coefficient β of SEST and VBT grown PPN single crystal were evaluated by the measurements of Z-scan using He–Ne laser beam with wavelength 632.8 nm and beam diameter of 0.5 mm respectively.

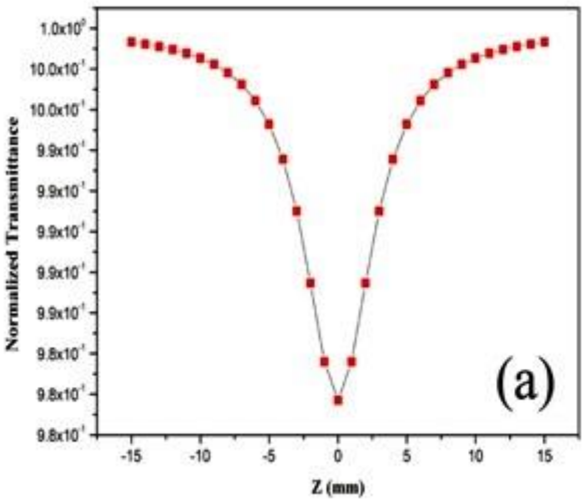
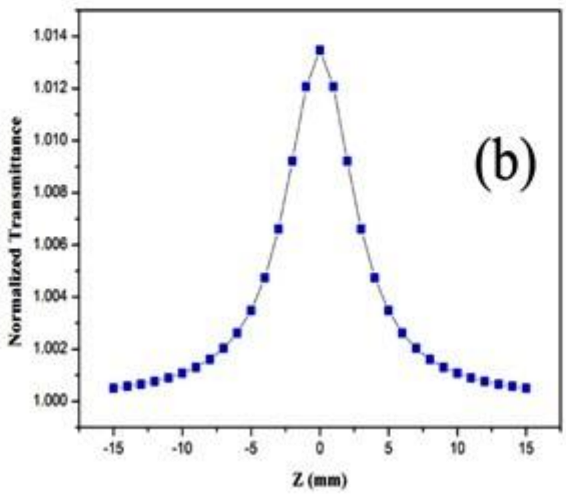


Fig. 2(a) open aperture of SEST PPN



(b) Open aperture of VBT PPN .

The input laser beam was converted into Gaussian form by focusing the laser beam with the Gaussian filter. The Gaussian beam TEM_{00} mode was allowed to pass through the convex lens (focal length of 30 mm) and the focal length of the convex lens vary depends on the incident Gaussian beam. At the focal length of 12.05 mm, the diameter of the Gaussian beam waist ω_0.

In order to vary the incident intensity falling on the sample, the sample crystal was passed from the +Z to – Z axial direction by using stepper motor. The digital power metre (Field master GS-coherent) was used to measure the transmittance intensity of the sample. By using open and closed aperture Z-scan measurement methods, the non-linear absorption and non-linear refraction quantity of the SEST and VBT grown PPN crystal was measured with the strict focusing geometry and it is shown Fig 2(a, b) and 3(a, b). The refracted laser beam was entirely absorbed by the detector in the open aperture method. Based on the diameter of the laser beam, the size of the aperture is reduced in the closed aperture method. When the input intensity through the far field aperture increases, the transmittance with low-beam divergence also increases, which is a vital property for optical limiting applications.

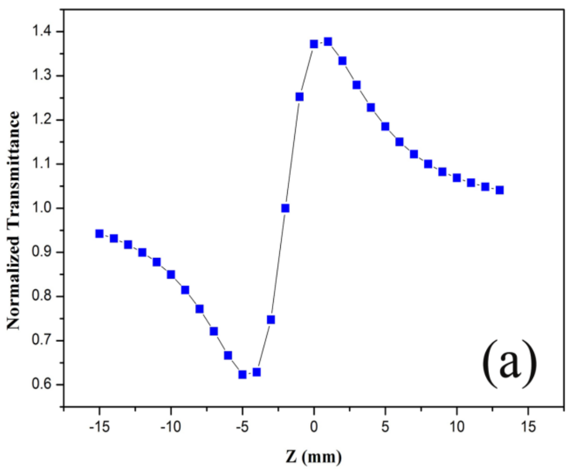
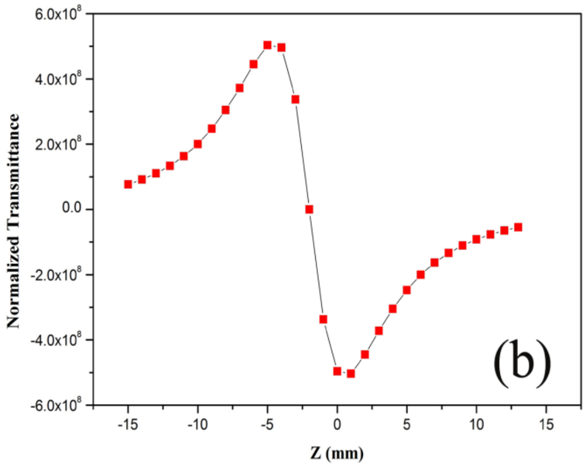


Fig.3 (a) Self-focusing effect of SEST PPN crystal in closed aperture

Fig 2(a) shows the open aperture Z-scan curves, which reveals an increase in the input intensity with the decrease in transmission. The curve also indicates the presence of reverse saturable absorption (RSA) (excited state absorption) with a positive non-linear absorption coefficient. The RSA property of the crystal material leads to optical limiting applications [8]. The absorption of the molecules in the excited state is comparatively high than in the ground state, which is termed as Reverse saturable absorption (RSA) [9].



(b) Self-defocusing effect of VBT PPN crystal in closed aperture

Fig .2(b) shows the absence of reverse saturation absorption (RSA) with the enhanced transmission towards the focal point which was identified through the open aperture scan method. It also demonstrates the strong saturation of absorption (SA) process. It is an obligatory parameter of a material which is useful for the laser applications such as laser pulse compression, laser pulse narrowing, and optical switching applications [10-12].

Fig. 3 (a) shows the valley followed peak configuration by the closed aperture method. The title crystal possesses a positive sign of third-order non-linear refractive index which was clearly suggested from the valley and peak configurations and also reveals the self-focusing effect.

Table-1 SEST PPN and VBT single crystal measurement details of Z-scan experiment

Measurement details of Z-Scan experiment	SEST	VBT
Laser beam wavelength (λ)	632.8 nm	632.8 nm
Focal length of lens	30 mm	30 mm
Optical path length	75 cm	75 cm
Beam radius of the aperture (w_a)	3.5 mm	3.5 mm
Aperture radius (r_a)	2 mm	2 mm
Sample thickness (L)	0.50 mm	0.50 mm
Beam radius (Wo)	6.03X 10^{-6}	6.03X 10^{-6}
Effective thickness (L_{eff})	0.4940 33 mm	0.4940 33 mm
Linear absorption coefficient (α)	0.125399962	0.125399962
Linear transmittance (S)	0.15	0.15
Nonlinear refractive index (n_2)	1.01 X 10^{-11} m^2/W	1.43 X 10^{-11} m^2/W
Nonlinear absorption coefficient (β)	5.97 X 10-5 m/W	8.11 X 10^{-5} m/W
Real part of third order susceptibility [Re (χ3)]	7.0295 X 10-6esu	9.682 X 10^{-6}esu
Imaginary part of third order susceptibility [Im (χ3)]	2.09201 X 10-6esu	2.76024 X 10^{-6}esu
Third order nonlinear susceptibility (χ^3)	7.33421 X 10-6esu	1.00678X 10^{-5}esu

Fig.3 (b) shows the closed aperture trace with a peak followed by a valley. It indicates the negative non-linear refraction of the sample crystal which leads to self-defocusing effect [13]. The local variation of the refractive index in terms of temperature is depends on the self-defocusing effect of the material. The self-defocusing effect of the crystal is a crucial feature in the applications such as night vision devices in order to protect the optical sensors [14, 15].

Table 1shows the experimental details and results of the Z-scan technique for PPN crystal grown by using SEST and VBT. From the above analysis, it was concluded that the PPN crystal grown from melt-grown technique reveals high value when compared to the other crystals.

4. CONCLUSION

Piperine single crystals are grown using slow evaporation solution growth technique and Vertical Bridgman Technique. piperine crystallises in a monoclinic system. The third order nonlinear susceptibility of VBT grown piperine crystal is higher than SEST grown piperine single crystal.

5. ACKNOWLEDGEMENT

The authors are grateful to the management of VIT University, Vellore for their excellent research facilities.

References

[1] Muthuraja, A., & Kalainathan, S. (2017). A study on growth, optical, mechanical, and NLO properties of 2-Mercaptobenzimidazole, 2-Phenylbenzimidazole and 2-Hydroxy benzimidazole single crystals: A comparative investigation. *Materials Technology*, *32*(6), 335-348.

[2] Muthuraja, A, Murugesan, G, Reeta Felscia, U, Beulah , J.M. Rajkumar, Kalainathan, S, and Ratcagar, V, et al. Experimental and Computational investigations of4, 4' Dimethoxybenzoin single crystal for optical limiting applications. Journal of Crystal Growth. (2022); ():126602 doi:10.1016/j.jcrysgro.2022.126602 https://www. sciencedirect.com/science/article/pii/S0022024822000902 .

[3] Muthuraja, A., Bharath, D., Murugesan, G., Anbuselvi, D., & Kalainathan, S. (2022). Nonlinear optical studies on bioperine crystals grown by vertical Bridgman technique for photonic applications. *Optics & Laser Technology*, 107639. [4] Rai, R. N.; Varma, K. B. R. *J. Cryst. Growth* 2005, *285*, 111-116.

[4] Muthuraja, A., & Kalainathan, S. (2015). Growth of organic benzimidazole (BMZ) single crystal by vertical Bridgman technique and its structural, spectral, thermal, optical, mechanical and dielectric properties. *Optical Materials*, (47), 354-360.

[5] Muthuraja A, Kalainathan S. Study on growth, structural, optical, thermal and mechanical properties of organic single crystal ethyl p-amino benzoate (EPAB) grown using vertical Bridgman technique. 2017;459:31-37.

[6] Muthuraja, A., Subramaniyan@ Raja, R., & Bharath, D. (2019). Growth and characterization of Piperine (PPN) single crystal grown by slow evaporation solution growth technique. *Materials Research Innovations*, *23*(4), 228-232.

[7] Muthuraja, A., & Kalainathan, S. (2017). Growth, hardness and laser damage threshold studies on vertical Bridgman grown piperine (PPN) single crystal. *Materials Research Innovations*, *21*(1), 50-54.

[8] F. Z. Henari, W. J. Balua, L. R. Milgrom, G. Yahyoglu, D. Philips and J. A. Lacey, Chem. Phys. Lett., 1997, 267, 229.

[9] F. Z. Henari, J. Opt. A: Pure Appl. Opt., 2001, 3, 188.

[10] X.-B. Sun,Y.-L. Wang, Q. Ren, Fu-jun Zhang, Y. Gao, H.-L. Yang, L. Feng, X.-Q. Wang and D. Xu, Opt. Mater., 2007, 29, 1305–1309.

[11] L. Irimpan, A. Deepthy, B. Krishnan, L. M. Kukreja, V. P. N. Nampoori and P. Radhakrishnan, Opt. Commun., 2008, 281, 2938–2943.

[12] V. P. N. Nampoori and P. Radhakrishnan, Opt. Commun.,2008, 281, 2938–2943

[13] Muthuraja, A., & Kalainathan, S. (2016). 9, 10-diphenylanthracene (DPA) single crystals grown by conventional slow evaporation method and its characterisation. *Materials Research Innovations*, *20*(5), 358-364.

[14] C. Vesta, R. Uthrakumar, B. Varghese, S. Mary NavisPriya, S. Jerome Das, J. Cryst. Growth 311 (2009) 1516–1520.

[15] Y.S. Zhou, E.B. Wang, J. Peng, J. Liu, C. Hu, R. Huang, X. You, Polyhedron 18 (1999) 1419–1423.