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RESEARCH ARTICLE

Synthesis, Characterisation of Novel NLO Material: bis-*L*-Phenylalanine Mandelate

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Abstract: Organic non-linear optical salt bis-*L*-phenylalanine mandelate (BLPAMA) was synthesized and single crystal was grown using slow evaporation method in water. Single crystal XRD revealed that the grown crystals belong to monoclinic system with space group $P2_1$. The intra molecular and inter molecular hydrogen bonding present in the molecular sheet stabilizes three dimensional network present in the BLPAMA compound. The ^{1}H NMR and ^{13}C NMR studies confirmed in the structure of the compound. Functional groups in the compound were identified using FTIR spectrum. Thermal stability of the compound BLPAMA from TG-DTA analysis correlate with the melting point of the compound, mass analysis confirmed the mass of the material, UV-Visible absorption and photoluminescence study of the compound indicated the suitability NLO activity. NLO activity of the compound was studied, revealed the presence of second harmonic generation.

Keywords: BLPAMA, Single crystal XRD, NLO activity, Second harmonic generation

Introduction

Alpha hydroxy aromatic carboxylic acid, mandelic acid a well-known skin care cosmetic ingradient posses conductivity property due to the presence of high polarisability. Amino acid, *L*-phenylalanine which produces useful salts by the zwitter ionic form of amino group and carboxylic acid group in it gave an idea to synthesize the compound BLPAMA and performed the characterization study of the novel NLO material.

Experiment

The compound BLPAMA was synthesized by the chemical reaction of commercially available 99% pure Alfa Aesar DL- Mandelic acid and Nice chemicals *L*-phenylalanine taken in the molar ratio 1:2 respectively by dissolving the mixture in water in a beaker, stirred well in a magnetic stirrer[1]. The solution was filtered and kept for slow evaporation at room temperature.

$C_6H_5CH(OH)COOH + 2\ C_6H_5CH_2CH(NH_2)COOH + H_2O$
DL- Mandelic acid *L*-phenyl alanine
↓
$C_6H_5CH(OH)COOH.(C_6H_5CH_2CH(NH_2)COOH)_2.H_2O$
Bis-*L*-phenylalaninemandelate (BLPAMA)

Single crystals formation was noticed after eight days and harvested crystals after 28 days. The compound BLPAMA was subjected to various characterisation studies. The structural, thermal, optical and fluorescent properties, XRD study and NLO studies and the results obtained were discussed in this paper.

Single crystal x-ray diffraction studies

The single crystal x-ray diffraction measurements were done using a Bruker AXS Kappa APEX II single crystal CCD diffractometer equipped with graphite -monochromated MoKα radiation wavelength 0.71073 Å with a dimension of 0.250*0.200*0.150 mm^3. Accurate unit cell parameters were determined from the reflections of 17546 in all the three crystallographic axes. The data collection, reduction and absorption correction were performed by APEX2, SAINT plus and SHELXL97. The final refinement coverges to an R-values of R=0.0346 and WR2=0.0807. The ORTEP drawing was performed with the ORTEP3 program[2].

The crystallographic refinement parameters were listed in Table 1. The compound BLPAMA crystallized in monoclinic space group $P2_1$. The structure was resolved in non-centero symmetric space[3] group $P2_1$. The present unit cell was indexed to a standard setting of a= 5.4369 (6) Å, b= 16.278(2) Å, c= 14.2654 (17) Å and V=1257.5 $Å^3$. The decrease in bond lengths of C-C, C-O, C-N and the decrease in bond angles between O-C-C, N-C-C, C-N-H were observed and the atomic displacement parameters of the disordered components were made similar using suitable similarity restraints[4,5]. In BLPAMA unit cell two *L*-phenyl alanine, one mandelic acid and one water molecules were found as in Figure 1.

Table 1. Crystal data and structure refinement for bis-*L*-phenyl alanine mandelate (BLPAMA)

Identification code	BLPAMA
Empirical formula	$C_{26}\ H_{32}\ N_2\ O_8$
Formula weight	500.53
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
a = 5.4369(6) Å	α= 90°.
b = 16.278(2) Å	β= 95.110(5)°.
c = 14.2654(17) Å	γ = 90°.
Volume	1257.5(3) $Å^3$
Z	2
Density (calculated)	1.322 mg/m^3
Absorption coefficient	0.098 mm^{-1}
F(000)	532
Crystal size	0.250x0.200x0.150 mm^3
Theta range for data collection	2.502 to 24.993°.
Index ranges-5<=h<=6, -19<=k<=19, -16<=l<=16	
Reflections collected	17546
Independent reflections	4430 [R(int) = 0.0446]

Completeness to theta = 24.993°	99.8 %
Absorption correction	
Semi-empirical from equivalents	
Max. and min. transmission	0.989 and 0.967
Refinement method	
Full-matrix least-squares on F^2	
Data / restraints / parameters	4430 / 4 / 358
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	
R1 = 0.0346, wR2 = 0.0715	
R indices (all data)	R1 = 0.0542, wR2 = 0.0807
Absolute structure parameter	-0.2(5)
Extinction coefficient	0.010(2)
Largest diff. peak and hole	0.141 and -0.135 e.$Å^{-3}$

The molecular structure of BLPAMA indicates the presence of the intra molecular hydrogen bonding interactions between amino groups of *L*-phenyl alanine, carboxyl group of mandelic acid and water molecule were shown in Figure 2.

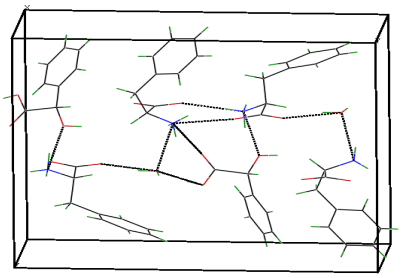

Figure 1. Unit cell of BLPAMA

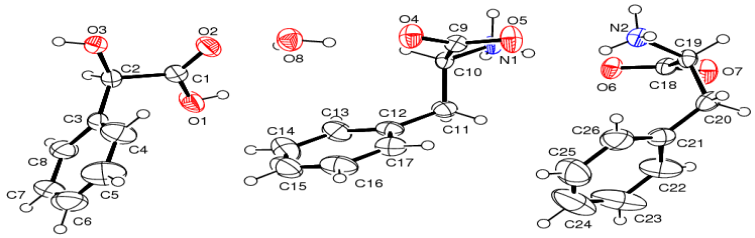

Figure 2. ORTEP diagram of BLPAMA

The molecular packing in the crystal was primarily decided by N-H..O and C-H...O hydrogen bonds, the bonds N1-H1A...O4, N1-H1A...O2 and N1...H1B...O3 intra molecular hydrogen bonding form a molecular sheet. The presence of O-H...0 hydrogen bond in the O8-H8A...04, O3-H3A...O7, O8-H8B...O2 molecular sheet due to the intra molecular and inter molecular hydrogen bonds Figure 3. Stabilises a three dimensional network which constitute the molecular packing in the crystalline solid[6-8].

The non-centrosymmetric crystal information of BLPAMA given in CCDC no. 1420631 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data-request/cif, by e-mailing data-request@ccdc.com.ac.uk or by contacting the Cambridge crystallographic data centre, 12 union road, Cambridge CB21 EZ, UK;fax:+44 1223 336033.3.2.

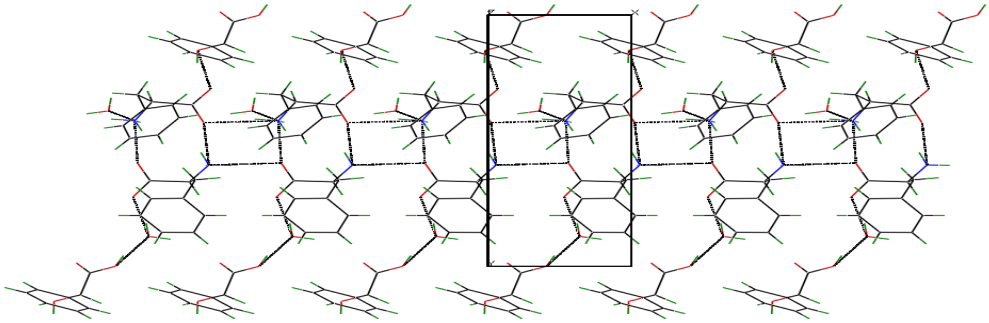

Figure 3. Hydrogen bonding in BLPAMA

Fourier transform infrared spectroscopy

The FTIR spectrum of BLPAMA crystals was recorded to study the functional groups in the sample. The absorption peaks at 3250-2800 cm^{-1} corresponds to N-H carbonyl, phenyl groups strong stretching vibrations[9], the presence of >C=O group was confirmed by strong stretching at 1711 cm^{-1}, the aromatic C=C stretching vibrations peak at 1600 cm^{-1} and intramolecular hydrogen bonding at 3300 cm^{-1} as shown Figure 4.

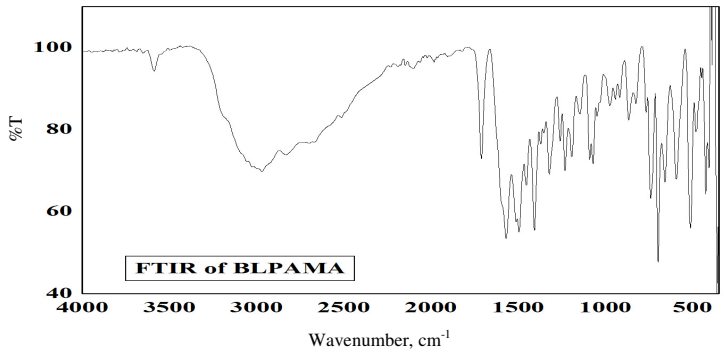

Figure 4. FTIR spectrum of BLPAMA

NMR spectral analysis

The ^{1}H and ^{13}C NMR spectra of BLPAMA were recorded in D_2O as solvent. In the Proton ^{1}H NMR Figure 5, NH proton at 3.8 ppm, CH_2 protons of the phenyl alanine group at 3.2 ppm, the OH proton at 5.3 ppm, the aromatic protons at 7.3-7.5 ppm were observed[10].

In ^{13}C NMR Figure 6, the carbonyl carbon atoms at 176 and 178 ppm, **t**he aromatic carbons at 127-139 ppm, presence aliphatic carbon atoms at 38, 58 and 75 ppm, confirmed the structure of the compound BLPAMA.

UV-Visible absorbance spectral analysis

The UV-Visible absorbance spectrum of BLPAMA crystal showed the crystal has sufficient transmission in the UV and visible region. The cut-off wavelength of BLPAMA crystal was found to be 240 nm Figure 7. The peak at 213 nm is due to $\pi \rightarrow \pi^{*}$ transition and the conjugated system present in the grown crystal[11]. The absence of absorption in the entire visible region indicates the crystal has suitable opto electronic applications.

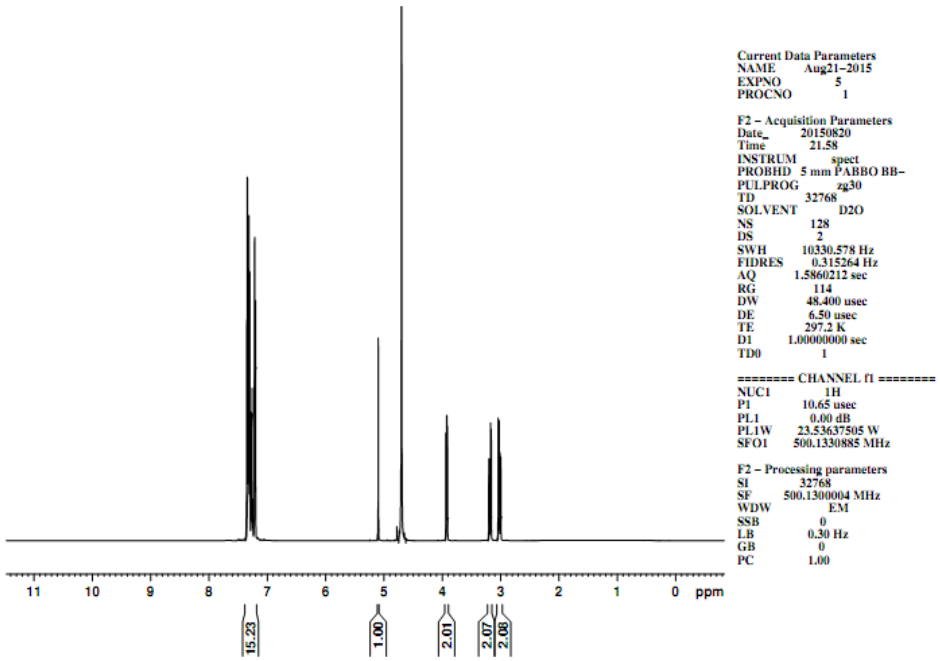

Figure 5. Proton NMR spectrum of BLPAMA

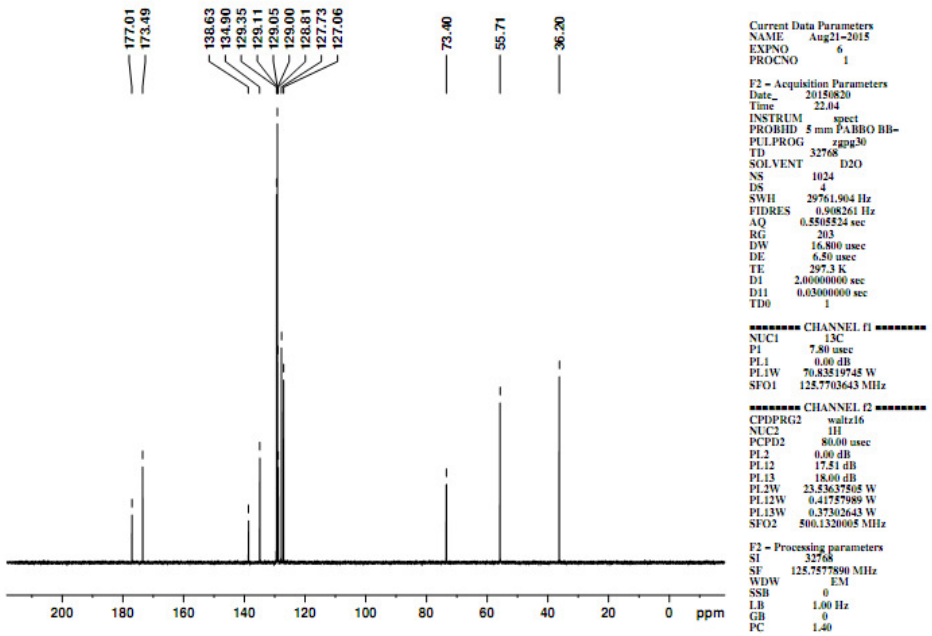

Figure 6. Carbon NMR spectrum of BLPAMA

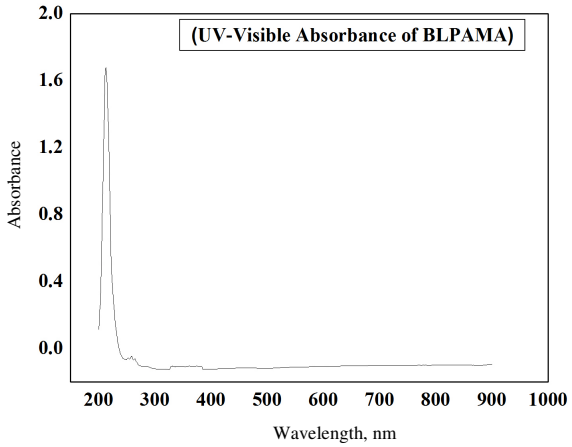

Figure 7. UV-Visible spectrum of BLPAMA

Fluorescence analysis

The excitation and emission spectrum was recorded in the range of 200-800 nm using water and methanol as solvent respectively[12]. The collisions and electrostatic interactions around solvent molecules broaden the vibrational transition along with electronic transition. Highly polar solvent methanol showed higher excitation and emission compared to water Figure 8.

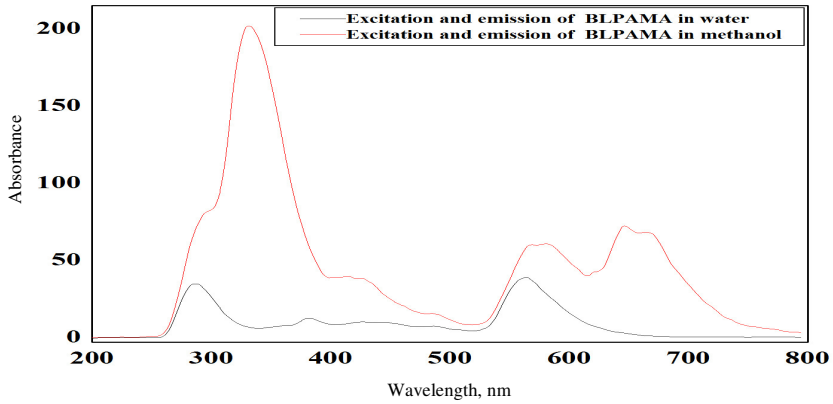

Figure 8. Fluoresence spectrum of BLPAMA in water and methanol

Mass spectrum

The BLPAMA compound confirmed the mass of the compound as 500 g from the mass analysis Figure 9.

Thermal studies

A powdered BLPAMA sample weighing 5.129 mg was used for the analysis. The TGA thermogram showed a three stage decomposition and an inflection point at 190˚ C corresponds to the onset of material decomposition, the melting point of the material was 184 ˚ C, confirmed the thermal stability of the crystal and supports the utility for NLO applications. The presence of water of crystallization in the molecular structure is indicated by the curve starting the weight loss around 100 ^{o}C in Figure 10.

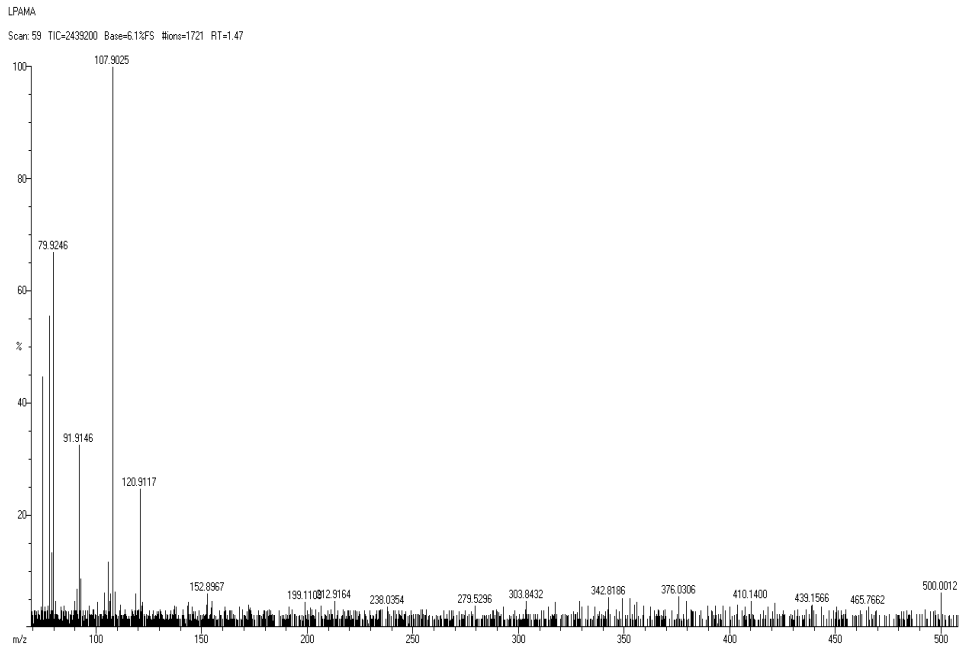

Figure 9. Mass spectrum of BLPAMA

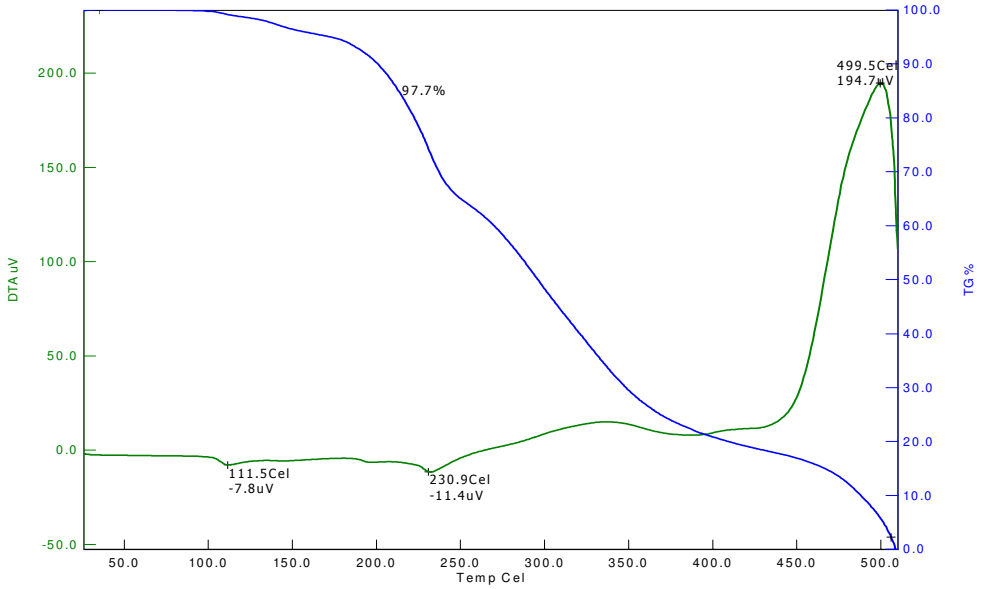

Figure 10. The TG-DTA of BLPAMA

Nonlinear optical studies

The second order nonlinear optical property of BLPAMA crystal was carried out using Q-switched high energy Nd:YAG Laser. Compared the NLO and SHG efficiency of the compound BLPAMA with that of KDP and found[13-15] it was 56%.

Conclusion

Crystalline multiple component organic salt BPLAMA was synthesized and single crystals were grown using the slow evaporation solution growth technique. Confirmed the structure with single crystal XRD analysis, functional groups using FTIR and NMR studies, mass analysis confirmed the molecular weight of the crystal, melting point supports the thermal stability of the compound BLPAMA and was confirmed by TG-DTA analysis. The optical behavior was evaluated by UV-Vis and photoluminescence analyses which substantiate the suitability of BLPAMA for opto -electronic applications. The presence of second harmonic generation was confirmed by the measurement of NLO activity.

Ackowledgements

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References

1. Xuan-Hung Pham, Jong-MinKim, Sang-Mok Chang, In-ho Kim, Woo-Sik Kim, *J Molec Catal B: Enzym.,*2009, **60(1-2)**, 87-92; DOI:10.1016/j.molcatb.2008.12.023
2. Ruby A and Alfred S, *Cecil Raj Adv Appl Sci Res*., 2012, **3(3)**, 1677-1685.
3. Selvakumar E, Anandhababu G, Ramasamy P, Rajnikant, Umadevi T, Meenakshi R and Chandramohan A, *Spectrochimica Acta A; Mol Biomol Spectros*., 2014,**125**, 114-119; DOI:10.1016/j.saa.2014.01.035
4. Chandramohan A, *Experiment*, 2014, **25(4),** 1759-1774.
5. Arunkumar A, Ramasamy P, *J Crystal Growth,* 2014, **388**, 124-131; DOI:10.1016/j.jcrysgro.2013.10.005
6. Robila K Mughal, Robin G Pritchard and Roger J, *Davey Acta Cryst*., 2004, **E60**, 1984-1986.
7. Laura Bereczki, Katalin Marthi and Gyorgy Pokol, *Per Pol Chem Eng*., 2009, **53(2)**, 71-76; DOI:10.3311/pp.ch.2009-2.07
8. Nikoletta B Bathori, Luigi R Nassimbeni and Clive L Oliver, *Chem Commun*., 2011, **47**, 2670-2672; DOI:10.1039/C0CC04279J
9. Natarajan V, Kalyana Sundar J, Selvarajan P, Aravindhan M, Sankaranarayanan K, Natarajan S and Hayakawal Y, *JMMC.,* 2011, **10**, 1.
10. Alosious Gonsago C, Helen Marina Albert, Janarthana S, Joseph Arul Pragasam A, *Int J Appl Phys Mathema*., 2012, **2**, 422.
11. Silambarasan A, Rajesh P and Ramasamy P, *Che Sci Rev Lett*., 2014, **2(6)**, 521-525.
12. Colin D McGuinness, Alexander M Macmillan, Kulinder Sagoo,d David McLoskey and David J S, *Birch Appl Phys Lett*., 2006, **89(6)**, 063901.
13. Sandhya Ravi, Chenthamarai S and Jayavel R, *IOSR-JAP*, 2015, **7**, 39.
14. Lawrence M and Felicita Vimala J, *IJESIT,* 2015, **4**, 208-214.
15. Puhal Raj A and Ramachandra Raja C, *Photonics Optoelectronics*, 2013, **2**, 56-64.