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Determination of nonlinear absorption (β) and refraction (n_2)by the Z-scan method: third-order nonlinear optical properties of π-conjugated Potassium Pentaborate crystal

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Abstract: *Potassium Pentaborate nonlinear optical (NLO) material was synthesized by the solution growth method. The grown crystals were subjected to structural, optical and mechanical property studies. Crystal with excellent transparency were grown with maximum size of 9mm×8mm×5mm and the grown crystals were characterized by single crystal Single crystal XRD, FT-IR, TGA-DTA&DSC, and UV–vis-NIR studies. The crystal belongs to orthorhombic with a space group of mm_2 having unit-cell dimensions a = 11.068Åb= 11.175Å c = 9.058Åand α = 90°; β = 90°; and γ =90°; Z=4, at 298(2) K. The second-order nonlinear optical property of the polycrystalline sample has been confirmed by Kurtz-Perry powder SHG analysis. Third order nonlinear optical properties were also studied by Z-scan techniques. Nonlinear absorption and nonlinear refractive index were found out and the third order bulk susceptibility of compound was also calculated.*

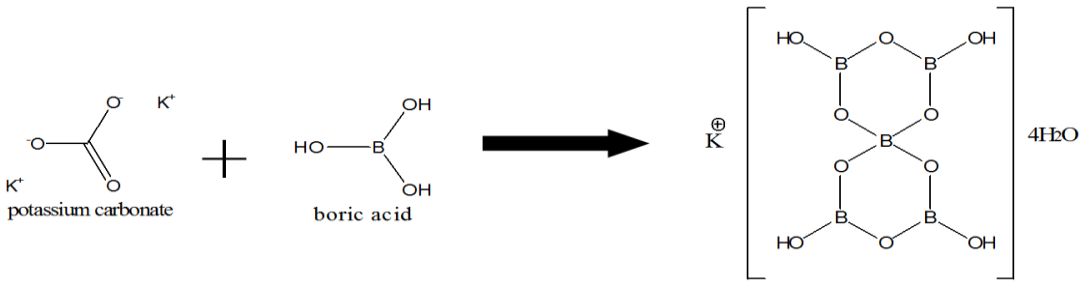
Keywords:*Single crystal X-ray diffraction; FTIR; UV-Vis-NIR; Thermal analyses; nonlinear optical material, Z-scan method.*

I. Introduction

The fast development in the field of optoelectronics has stimulated the search for highly new non-linear optical crystals for efficient signal processing. New non-linear optical frequency conversion materials can have a significant impact on laser technology, optical communication and optical data storage technology. Materials with nonlinear electro optic properties have a role in modern optoelectronics that is analogous to that of non-linear electronic circuit elements in conventional electronics. Inorganic borates exist in numerous structural types and some crystals such as Potassium pentaborateand BBO are excellent non-linear optical (NLO) materials, particularly in the UV region. These boratecrystals generally possess chemical stability, high damage threshold and high optical quality, as wellas wide range of transparency far into the ultraviolet on account of the rather large difference in the electronegativities of B and O atoms. The properties determining an effective NLO material particularly, the borate compound materials have been discussed by several researchers [1–6]. KB_5 crystal is un-colored, optically biaxial positive with optic plane 010 [7]. The growth of single crystals and twinned crystals of KB_5 by low temperature solution growth is reported by several workers [8-11]. Studies of pyroelectric properties, the influence of hydrostatic pressure on spontaneous polarization, electro-optic effect and spontaneous birefringence of potassium pentaboratetetrahydrate crystal are reported by Poprawski et al. [12]. In this paper, we describe the crystal structure, spectroscopic and thermal properties of the Potassium pentaborate. Freshly grown crystals were subjected to single-crystal X-ray diffraction, with the aid of Fourier transform infrared Spectroscopy (FTIR), DGA/DTA analyses and third order nonlinear optical z-scan measurements, the presence of various functional group, mechanical stability and second & third order nonlinearity of the sample have been assessed in detail.

II. Synthesis Of Potassium Pentaborate:

The potassium pentaborate (KB_5) was synthesized using boric acid (H_3BO_3) and potassium carbonate (K_2CO_3). Boric acid (H_3BO_3) and potassium carbonate (K_2CO_3) were taken in the stoichiometric ratio 10:1. The required volume of potassium carbonate (K_2CO_3) was dissolved with double distilled water. Then the calculated amount of boric acid (H_3BO_3) was slowly added in the solution. The reactants were thoroughly dissolved in double distilled water and stirred well using a temperature controlled magnetic stirrer to yield a homogeneous mixture of solution. Then, the solution was allowed for slow evaporation. Transparent crystalline salt of Potassium Pentaborate, get collected in the Beaker after few days[13-17]. The process of recrystallization was carried out to purify the synthesized salt. The reaction mechanism of Potassium Pentaborateis given in the Scheme and the crystal grown from slow evaporation technique is shown in Fig.1(a).



Schematic representation of potassium Pentaborate reaction

III. Characterization Studies:

The unit cell dimension and X-ray intensity data of $KB_5O_8H_4$.$4H_2O$ was obtained on a EnrafNonius CAD 4 Bruker Kappa APEX II single crystal X-ray diffractometer equipped with MoK_α radiation (λ=0.71073 Å). The FTIR spectrum of the title crystal was recorded in the frequency range 400-4000cm^{-1} using a Bruker IFS 66V FT-IR spectrometer by KBr pellet method to identify the various functional groups present in the title crystal. Optical absorptions properties of the crystals were studied using a Varian Cary 5E UV-Vis-NIR spectrophotometer.Simultaneous Thermo gravimetric (TGA) and differential thermal analyses (DTA) were carried out using Perkin-Elmer TGA 7thermal analyzer and differential scanning calorimeter were carried out using Perkin-Elmer DSC 7 calorimetric analyzer. Third order nonlinear optical measurement of the $KB_5O_8H_4$.$4H_2O$ crystal has been studied using versatile Z-scan techniques.

IV. Results And Discussion:

4.1 SINGLE CRYSTAL X – RAY DIFFRACTION:

The grown crystal was subjected to single crystal X-ray diffraction study at roomtemperature using BRUKER NONIUS CAD4 single crystal X-ray diffractometer with MoKα radiation (λ= 0.71073 **Å**). At room temperature KB_5 crystal belongs to orthorhombic system and the cell parameters are a = 11.068 Å, b = 11.175 Å and c = 9.058 Å, α = β = γ=90° and with unit cell volume V = 1116.38 (Å) ^{3} and these values match well with the corresponding values reported [4-8] given in parentheses.

4.2MORPHOLOGY STUDIES

The typical growth morphology of KB_5 single crystal is shown in Fig.1 (b). The crystal has twelve visible faces out of which four are well defined. They are (2 0 0) (0 0 -2) (1 3 -2) and (2 3 -1). Among them, (0 0 -2) is the smallest plane and (2 0 0) is the bigger plane. In the a-direction, (1 3 -2) and (1 3 2) are the prominent morphological planes. The a-direction (a-axis) is along the length of the crystal. The b-direction (b-axis) and c-direction (c-axis) are normal to (2 0 0) and planes and the c-axis also coincide with one of the edges of the crystal. Therefore it clearly suggests that the fastest growth occurs along the shortest crystallographic axis (a-axis) of the crystal.

4.3 FTIR VIBRATIONAL ANALYSIS:

Fourier transform infrared spectrum of the KB_5 sample was recorded in the range 400 – 4000 cm^{-1} by employing Bruker IFS 66V FT-IR spectrometer using KBr pellet method.The recorded FT-IR spectra of Potassium Pentaborate crystal is shown in Fig. 2the observed bands and their assignments are listed in Table 2. The frequency observed at 3061 and 3381cm^{-1} of KB_5 crystal attributed to OH stretching vibrations. A Peak at 1447 cm^{-1} and 1032 cm^{-1} in the IR spectrum is assigned to the B-O terminal Stretching. The absorptions 1250 cm^{-1}, 1108 cm^{-1} and 1353 cm^{-1} corresponds to the B-O asymmetric Stretching. The Peak at 780 cm^{-1} and 930 cm^{-1} are assigned to ring Stretching of B-O. In KB_5, the Peak at 703 cm^{-1} corresponds to O-B-O terminal bending vibrations. The sharp absorption at 508 cm^{-1} is assigned to O-B-O ring bending.

4.4 THERMAL ANALYSIS:

The TGA/DTA thermograms of the KB5 crystal obtained in the presence of nitrogen atmosphere with a heating rate of 10˚C/min are shown in Fig.3. There is a weight loss of about 12 % in first stage due to the release of two water molecules present in the crystal lattice. This is accompanied by major weight loss of KB_5 occurring in two stages between 137 and 300 °C. It may due to devoid of any detectable amount of adsorbed or lattice entrapped water. Above that temperature decomposition takes place. The DTA analysis shows an endothermic transition was also carried out in the same atmospheric condition. There is an endothermic transition between 137 and 205 °C which is good in agreement with the TGA trace. The sharp endothermic peak at around 205 °C is assigned to melting point of the title compound. Sharpness of the endothermic peak observed in DTA shows

good degree of crystallinity of the specimen. Hence it may be useful for making the NLO devices like second harmonic generator, frequency doublers below its melting point. There is a sharp endothermic peak at 203˚C in the DSC, which confirms the decomposition of the compound.

4.5 UV-VIS-NIR SPECTRAL ANALYSIS:

The UV-Visible NIR spectrum gives limited information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electron in σ and π orbital's from the ground state to higher energy states [13]. Transmittance spectra are very important for any NLO material because a nonlinear optical material can be of practical use only if it has wide transparency window. To find the transmittance range of KB_5, the optical transmittance spectrum for the wavelengths range between 200nm to 1200 nm was recorded. A crystal of thickness 1mm was used for this analysis. A graph of transmission versus wavelength is shown in Fig. 5.From the graph, it is evident that KB_5 crystal has a UV cut-off around 200nm which is sufficiently low for SHG laser radiation at 1064nm and sufficiently low for THG laser radiation at 632.8nm or other application in the blue region. It is optically transparent in the UV-Visible NIR region with 75% transmission level. There is no considerable absorption of light to any appreciable extent in the visible range of electromagnetic spectrum, which is the intrinsic property of all boric iron complexes.

4.6 Z-SCAN TECHNIQUE:

The third- order nonlinearity of Potassium Pentaborate single crystals samples were investigated from the Z- scan technique, a simple and accurate method to determine both the nonlinear index or refraction, n_2, and the nonlinear absorption coefficient, α_2. The Z-scan experimental setup details have been reported elsewhere and therefore, only a brief description is presented here. The Z-scan experiments were performed using a 632.8 nm He-Ne laser beam, which was focused by 20 cm focal length lens. The typical laser source and sample parameters used for the experiment are tabulated in Table.3. Basically, the method consists in translating the nonlinear sample through the focal plane of a tightly focused Gaussian beam and monitoring the changes in the far field intensity pattern. For a purely refractive nonlinearity, the light field induces an intensity dependent nonlinear phase and as a consequence of the transverse Gaussian intensity profile, the sample presents lens-like behaviour. The induced self-phase modulation has the tendency of defocusing or re-collimating the incident beam, depending on its Z position with respect to the focal plane. By monitoring the transmittance change through a small circular aperture placed at the far-field position, one is able to determine the nonlinear refractive index. Any nonlinear absorption present at the sample can be found from this measurement by removing the aperture (open aperture z scan) shown in Fig 6(a),(b)[19-23]. In this case, once the sample is scanned through the laser beam focal plane the sample transmittance is measured as function of the intensity. With this procedure we generate z scan signatures and the transmittance change between the peak and the valley ΔT_{p-v} can be extracted from them. Using the relation;

$$\Delta T_{p-v} = \frac{0.406\ (1-S)^{0.25}}{\Delta\phi_o} \quad \ldots\ldots\ldots \quad (1)$$

where$S = 1 - e^{\frac{-r_a^2}{\omega_a^2}}$ is the aperture linear transmittance, $\Delta\phi_o$ is the on-axis phase shift. The on-axis phase shift is related to the third-order nonlinear refractive index by

$$[\Delta\phi_o] = k n_2 L_{eff} I_o \ldots\ldots\ldots \qquad (2)$$

where $k = \frac{2\pi}{\lambda}$, $L_{eff} = \frac{[1-e^{-\alpha L}]}{\alpha}$ is the effective thickness of the sample, α is the linear absorption coefficient, L the thickness of the sample, I_o is the on-axis irradiance at focus and (n_2) is the third-order nonlinear refractive index.

The nonlinear absorption and refractive index of Potassium Pentaborate crystals (thickness ≈1.7mm) were estimated using the above formalism for the laser beam of intensity 60mW and of wavelength of 632.8 nm. Depending on whether nonlinear refraction is positive or negative the sample causes an additional focusing or defocusing. In the most reported experiments, 0.1 <*S* (transmittance) <0.5 has been used for determining nonlinear refraction. Obviously, the *S* = 1 corresponds to the collection of all transmitted light and therefore is insensitive to any nonlinear beam distortion due to nonlinear refraction [24-26]. Nonlinear refractive index (n_2) of KB_5 was calculated as 15.8770×10^{-7} cm^2/W and the value of nonlinear absorption coefficient has been measured from the open Z-scan as β~ 4.0128x 10^{-3} cm/W.

V. Conclusion:

Single crystals of potassium Pentaborate have been grown by slow evaporation as well as slowing cooling technique. The grown samples were characterized by various tools like Single crystal XRD, UV-Vis-NIR, FTIR, thermal, SHG and THG analysis. Single crystal XRD confirms that the material crystallizes in an orthorhombic crystal system with point group mm_2. UV-Vis-NIR studies reveals the wide transparency nature of the crystal FTIR studies confirm the various functional groups present in the crystal and vibrational structure of the compound has also been elucidated. Thermal analysis through DSC shows that the crystal is thermally stable up to 203°C. The third order nonlinear measurement using Z-scan techniques reveals the positive nonlinearity (self focusing) exhibited by the title compound. The nonlinear refractive and nonlinear absorption coefficient of the crystal at 632.8 nm has been found to be $n_2=15.8770\times10^{-7}cm^2/W$and $\beta\sim 4.0128x\ 10^{-3}cm^2/W$ respectively.

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FIGURE CAPTIONS

Fig.1. (a) KB_5 crystals grown from slow (b) Morphology of KB_5 single crystal
Fig.2. FTIR spectra of KB_5 single crystal
Fig.3. TG-DTA Curve of KB_5 single crystal
Fig.4. DSC curve of KB_5 single crystal
Fig.5. UV-Vis-NIR spectra of KB_5 single crystal
Fig.6. Schematic diagram of the Z-scan technique
Fig.7. (a) Closed aperture Z-scan signature of KB_5 single crystal(b) Open aperture Z-scan signature of KB_5 single crystal

Table 1: Unit cell parameters of $[K(H_4B_5O_{10})].4H_2O$

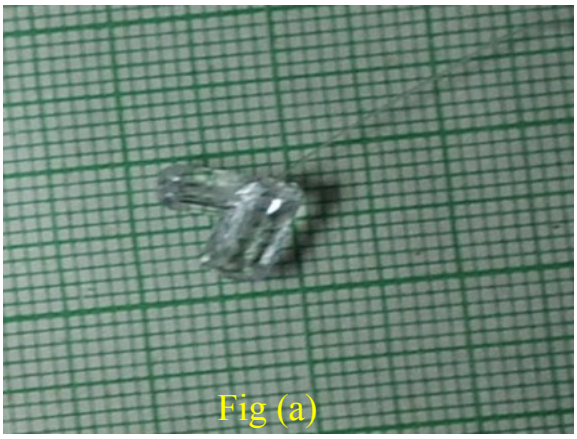
Empirical formula	$[K(H_4B_5O_{10})].4H_2O$
Formula Weight	293 g
Crystal space group	orthorhombic crystal systemwith point group mm2
Unit cell dimension	a = 11.068 Å b = 11.175 Å c = 9.058 Å and α = β = γ = 90°

Table 2: FTIR assignments of Potassium Pentaborate

Wave number (cm^{-1})	Assignments
508	OBO- ring bending
703	OBO - terminal bending
780	BO - ring stretching
930	BO - ring stretching
1032	BO - terminal stretching
1108	BO - asymmetric stretching
1250	BO - asymmetric stretching
1353	BO - asymmetric stretching
1447	BO - terminal stretching
2489	BH – boron octet stretching
3061	OH - stretching
3381	OH - stretching

Table.3. Laser source and sample parameters used for Z-scan experiment

S.No.	Parameter	Observed value
1.	Wave length of the source (λ)	632.8nm
2.	Laser power (P)	60mw
3.	Optical path length (L)	160cm
4.	Sample thickness (l)	1.70mm
5.	Beam radius (ω_L)	2mm
6.	Aperture radius of the detector (r_a) (1)closed aperture (2)open aperture	 4mm 20mm
7.	Beam radius at aperture (ω_a)	2mm
8.	Focal length of the lens	20cm
9.	Rayleigh length	7.320 mm



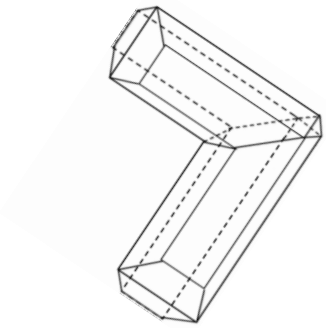


Fig (b)

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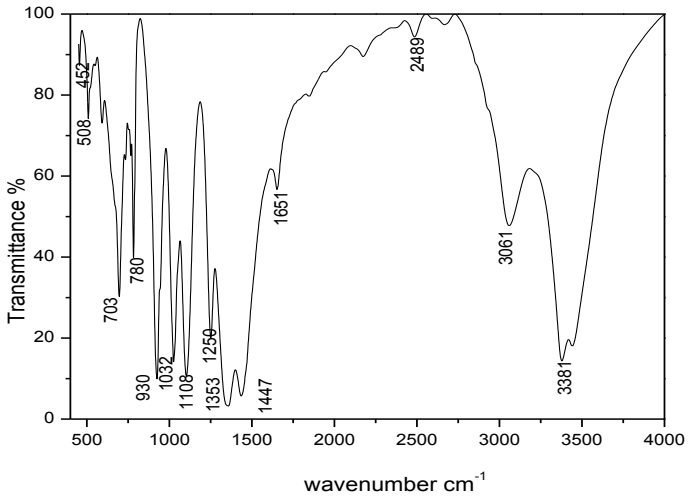

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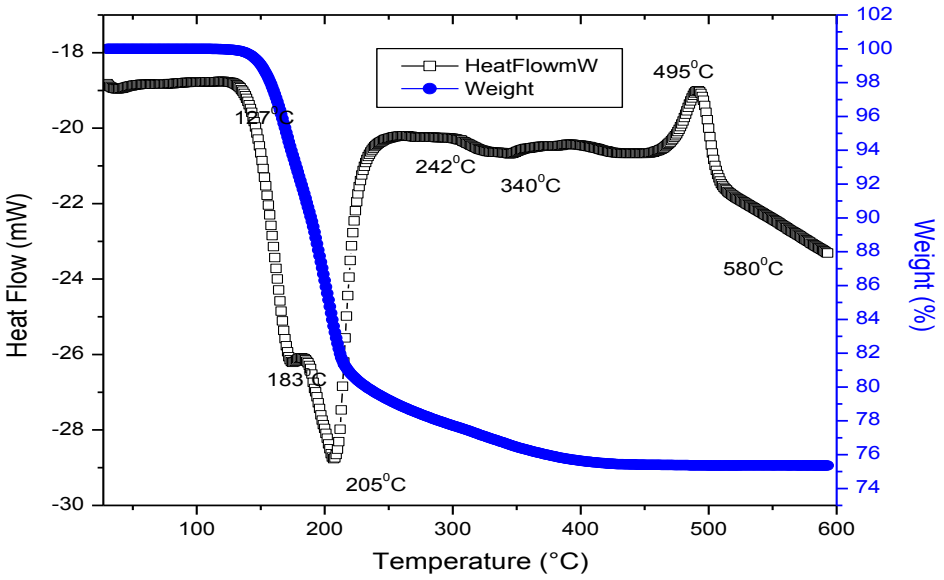

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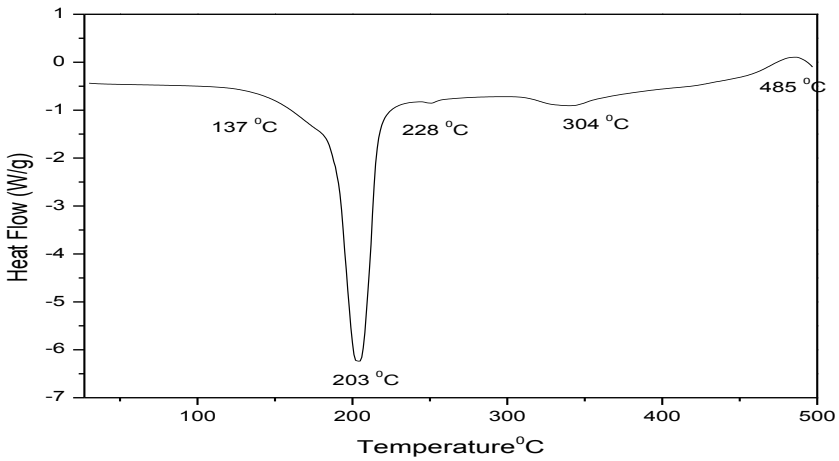

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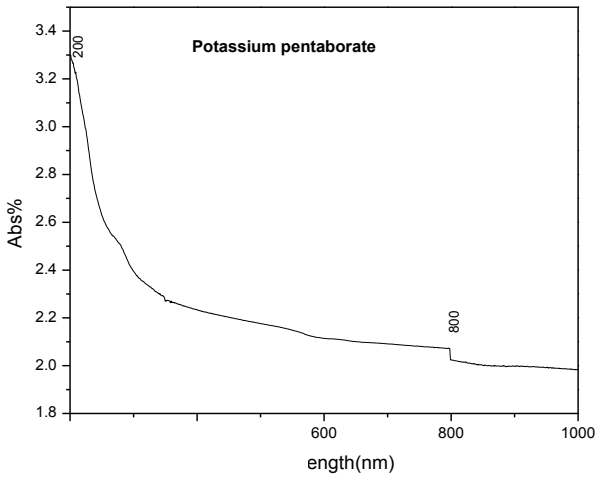

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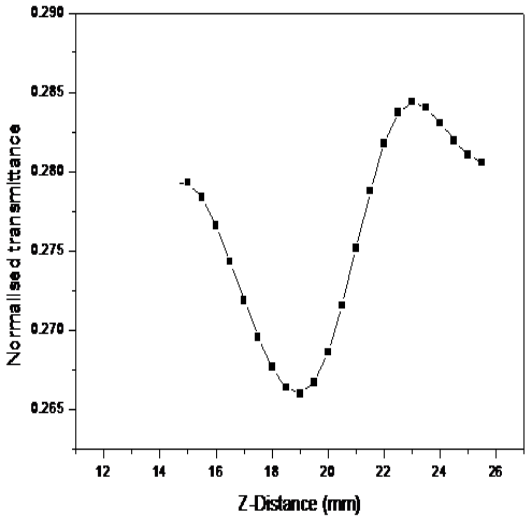

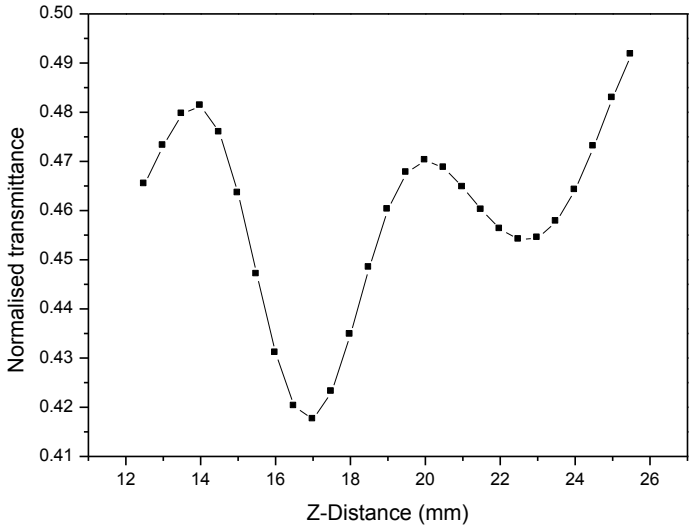

Fig.6. P.Arularasan et.al.,