

Optical and Mechanical Studies of 4-Chloro-3-Methylphenol Single Crystal

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Abstract- Single crystal of 4-Chloro-3-Methylphenol, an organic non linear optical material was grown from aqueous solution by low temperature solution growth technique with ethanol as a solvent. Good optical quality single crystal of dimensions 15 x 5 x 2 mm³ was harvested in a period of three weeks. The crystal system was confirmed from single crystal X-ray diffraction analysis. FTIR spectral analysis reveals the presence of functional groups present in the grown crystal. The optical behaviour of 4-Chloro-3-Methylphenol crystal was identified from UV-vis-NIR spectrum and the cut-off wavelength was found. Microhardness studies were carried out using Vickers pyramidal indentation method shows that the grown crystal belongs to soft material.

Key words: Xray diffraction, FTIR, UV analysis, microhardness studies

I INTRODUCTION

The nonlinear optical (NLO) materials capable of generating second harmonic have received a great deal of attention due to their commercial importance in the field of optical communications, signal processing, sensing and instrumentation [1]. The requirement of non-centrosymmetry for SHG has been successfully designed in different organic systems using a number of strategies. The most obvious is the use of a single enantiomer of a chiral component, which guarantees crystallization in an acentric space group [2]. In the last several years, organic NLO crystals have attracted much attention because of their superior properties, such as large susceptibility, faster response than their inorganic counterparts and the capability of designing on the molecular level. The organic compounds with electron sufficient (donor) and electron deficient (acceptor) counterparts, provide the asymmetric charge distribution in the π electron system and shows large non-linear optical responses. Organic nonlinear optical materials may be far superior to their inorganic counterparts, owing to the irrelatively high and faster nonlinearities [3,4]. Therefore, presently there is a need to produce high efficient NLO materials capable of generating blue light by second harmonic generation [5,6]. Crystal of 4-Chloro-3-Methylphenol (4C3MP) is a known organic material, it has a wide range of application. Since there is no report available on the growth of 4C3MP. We have reported the growth of 4C3MP crystal by slow evaporation technique using ethanol as solvent. The grown crystal were subjected to single crystal XRD, optical and mechanical studies. The results of the XRD studies which shows that 4C3MP belongs to monoclinic crystal system and space

group P2₁. The optical behaviour of 4C3MP grown crystal was identified from UV-vis-NIR spectrum and the cut-off wavelength was determined. Microhardness studies were carried out using Vicker's pyramidal indentation method shows that the grown crystal belongs to soft category.

II MATERIAL SYNTHESIS

The title compound 4-Chloro-3-Methylphenol was synthesised by dissolving C₇H₇ClO in ethanol. The aqueous solution was stirred for 4h and after stirring, the supersaturated solution was filtered with whatmann filter paper and kept in the dust free atmosphere. The saturated solution was allowed to dry at room temperature by the slow evaporation method. After a period of three weeks, optically transparent and defect free crystal was obtained with the dimensions of 15 x 5 x 2 mm³. The photograph of grown crystal was shown in Figure 1.



Figure 1. Photograph of an grown 4C3MP crystal.

III RESULTS AND DISCUSSION

A. Single crystal XRD

The grown crystals were subjected to single crystal X-ray diffraction using ENRAF NONIUS CAD-4 single-crystal X-ray diffract meter with MoK α radiation ($\lambda = 0.7170 \text{ \AA}$) to determine the unit cell dimensions. The pure crystal is found to be crystallized in the monoclinic system with space group P2₁. The cell parameters are listed in Table 1.

Table 1 .Unit cell parameters

Lattice parameters of 4-Chloro-3-Methylphenol	Crystal data
Molecular Formula	C ₇ H ₇ ClO
System group	Monoclinic System
Space group	P 2 ₁
a	10.6998 (4) Å
b	14.2926 (5) Å
c	8.7105 (3) Å
α	90 ⁰
β	91.152 ⁰
γ	90 ⁰
Cell volume(V)	1331.81(8) Å ³

B. OPTICAL ABSORPTION STUDIES

The optical absorption spectrum of the grown crystals was recorded in the range 200-800 nm and the absorption spectrum is shown in Figure 2. From the UV absorption spectrum, it was found that there is very low absorbance in the entire visible region. Excellent optical transparency with the lower cut-off wavelength at 283 nm makes it as a potential material for device fabrication.

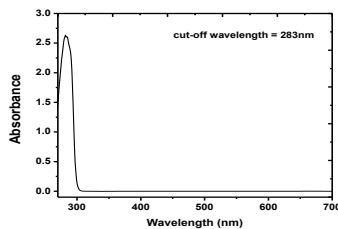


Figure 2. UV-VIS-NIR spectrum of 4C3MP single crystal

The optical band gap energy (E_g) was calculated using the relation

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu}$$

Where, hν-incident photon energy, α - absorption coefficient, E_g- optical band gap. The plot of variation of (αhν)² versus hν yields the band gap energy of 4.28eV for the grown 4C3MP crystal and it was depicted in figure 3.

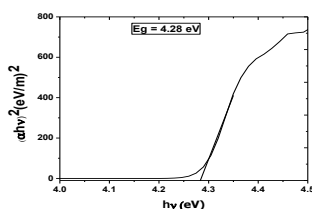


Figure 3. Plot of (αhν)² versus photon energy for 4C3MP

C. FTIR ANALYSIS

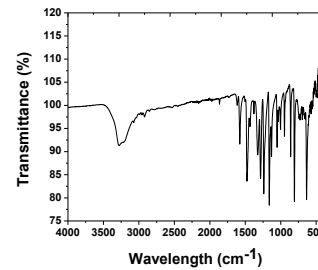


Figure 4. FTIR spectrum of 4C3MP crystal

The FTIR spectra of 4C3MP crystal was recorded in the range of 400-4000 cm⁻¹. The O–H group gives rise to three vibrations namely stretching, in-plane bending and out-of-plane bending vibrations. Hydroxyl group in the associated form absorbs at 3500–3300 cm⁻¹, the value of frequency shift in phenols derivatives depends on the strength of the H bonds and also the type of association. The weaker C–H stretching modes are generally superimposed upon the broad O– H band due to intermolecular hydrogen bridge. The visual inspection of observed spectrum in Figure. 4 of 4C3MP of validate the above facts. Phenols without bulky ortho groups, whether in concentrated solution or as solids or in the pure liquid phase, have a broad absorption at 3400–3230 cm⁻¹ [7]. Accordingly, in the present study the O–H stretching vibration is observed at 3280.73 cm⁻¹ in the FTIR spectrum , which is due to no bulky ortho groups. The frequency due to O–H in-plane bending vibration in phenols, in general lies in the region of 1150–1250 cm⁻¹ . The very strong FTIR band at 1324.55 cm⁻¹ of 4C3MP are attributed to this vibration. For the associated molecule the O–H out-of-plane bending mode lies in the region 572–728 cm⁻¹ [8]. In both the intermolecular associations, the frequency is at a higher value than in free O–H. The O–H torsional vibration is very anharmonic and hence it is difficult to reproduce this frequency with a harmonic approach. In our title molecule, the FTIR bands at 457 cm⁻¹ are assigned to O–H out-of-plane bending vibrations. C–O group vibration The most important contribution to C–O stretching modes appeared at 1239 cm⁻¹. These modes can be described as coupled vibrations, involving main contributions from the C–O stretch along with aromatic ring vibration [9]. The C– O out-of-plane vibrations have an important contribution to.

IV VICKER’S MICRO HARDNESS TEST

Measurement of hardness is a useful non destructive testing method used to determine the applicability of the crystal. Microhardness study was carried out on 4C3MP single crystal lusing a Vickers microhardness tester fitted with a Vickers diamond pyramidal indenter in order to evaluate its mechanical stability.

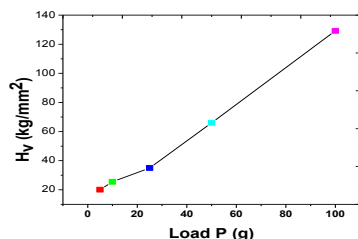


Figure 5. Variation of load with vicker's hardness number

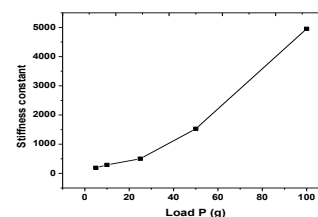


Figure 7 Plot of load P versus Stiffness constant

The static indentations were made at room temperature with a constant indentation time of 5 s for all indentations. A cut and polished sample of 4C3MP was used for the study. The indentation were made by varying the load from 5 to 100 g at room temperature. The Vicker's Microhardness number of the title crystal was calculated using the relation,

$$H_V = 1.8544 \left(\frac{P}{d^2} \right) \text{ (kg/mm}^2\text{)}$$

Where, 'H_v' is the Vickers hardness number, 'P' is the applied load and 'd' is the average diagonal length of the indentation mark.

Plots between hardness number and load for 4C3MP single crystals at room temperature is depicted in Figure 5. It is clear that the microhardness number increases with increasing load, which is in agreement with the reverse indentation size effect (ISE) [10]. The relation connecting the applied load and diagonal length d of the indenter is given by Meyer's law $P = ad^n$ [11], where the exponent 'n' called as the Meyer number, is the measure of the Indentation Size Effect (ISE) and 'a', is the constant 'd' is chordal diameter (diameter of the indentation). For the normal ISE behavior, the exponent $n < 2$. When $n > 2$, there is the reverse ISE behaviour. When $n = 2$, the hardness is independent of the applied test load, and is given by Kick's law [12].

Plots obtained between log(P) and log(d) for 4C3MP single crystal at room temperature is a straight line and is shown in Figure. 6. The value of 'n' obtained for 4C3MP single crystal using linear fit is found to be 1.82 respectively. This is also in good agreement with RISE [10]. On careful observations made on various materials, Onitsch and Hanneman [13] pointed out that 'n' lies between 1 and 1.6 for hard materials, and if it is more than 1.6 for soft materials.

An elastic stiffness constant or simply an elastic constant measures how "hard" a solid is. An elastic stiffness constant (C₁₁) for the title compounds were calculated using the Wooster's empirical formula $C_{11} = H_V^{7/4}$. The plots of stiffness constant versus load P are shown in Figure 7. The trend of stiffness constant graph is similar to hardness number graph which gives an idea about tightness of bonding between neighbouring atoms [14].

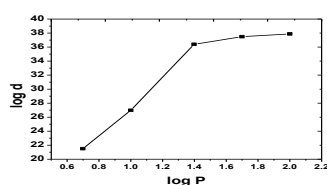


Figure 6 Plot of log P versus log d

V CONCLUSION

Optically good quality single crystal of 4C3MP was grown by slow evaporation technique using an ethanol as a solvent. The findings are concluded as follows, Single crystal X-ray analysis confirms that the crystal belongs to the monoclinic system with space group P2₁, and lattice parameters a=10.6998 Å, b=14.2926 Å, c=8.7105 Å and α=β=γ=90 Å. FTIR spectral analysis confirms the presence of functional groups. The cut off wavelength for the 4C3MP crystal is about 283 nm and the band gap was found to be 4.28 eV from the UV-Vis analysis. Mechanical hardness studies reveal that Vickers hardness number decreases as the load increases and work hardening coefficient was found to be 1.82 and it reveals that the grown crystal belongs to soft material.

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VII REFERENCES

- [1] D.F. Eaton, Science 253{1992} 281 – 287
- [2] C.B. Aakeroy, P.B. Hitchcock, K.R.Seddon, J. Chem. Soc., Chem. Commun.7{1992} 553 – 555.
- [3] L. Dalton, Adv .Polym. Sci., 158 (2002)1.
- [4] G.R. Meredith, Nonlinearoptical properties of organic and polymeric methods, in: J.Williams (Ed.) , ACS Symposium Series 223, American Chemical Society, Washington, DC,(1983).
- [5] J. Zyss, J.F. Nicoud, M. Coquillay, J.Chem. Phys. 81 {1984} 4160.
- [6] C.Razzetti, M.Ardoino, I.Zanotti, M. Zha, C.Parorici , Cryst. Res. Tech- nol. 37 {2002} 456.
- [7] George. Socrates, Infrared and Raman Spectroscopy Characteristic Group Frequencies, Table and Charts, Third ed., John Wiley & Sons, Ltd., New York, 2001. pp. 99.
- [8] Y. Morino, T. Shimanouchi, IUPAC Commission on Molecular Structure on Spectroscopy, Pure Appl. Chem. 50 (1978) 1707–1713. [32] N.B. Colthup, L.H. Daly, S.E. Wiberley, Introduction to Infrared and Rama
- [9] Vasile Chis, Chem. Phys. 300 (2003) 1
- [10] K. Sangwal, Cryst. Res. Technol.,44 (2009) 1019.
- [11] K. Sangwal, B. Surowska, P. Blaziak, Mater. Chem. Phys.,80 (2) (2003) 428.
- [12] D. Tabor, 'The Hardness of Metals', Clarendon Press, Oxford, UK, 1951.
- [13] E.M. Onitsch, Mikroskopie,2 (1947)131.
- [14] W.A. Wooster, Rep. Prog. Phys.,16 (1953) 62.