Spectral and Thermal Studies of Gel Grown Benzophenone Crystal

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***Abstract*—Benzophenone has significant relevance in non linear optical applications. Benzophenone crystals had already been grown by several methods. In this work, single crystals of benzophenone were successfully grown by gel method. The single crystal X ray diffraction technique was carried out to obtain the crystallographic data from which valence electron plasma energy and Fermi energy was also calculated. The grown crystal was subjected to FTIR spectral analysis to confirm the presence of functional groups. The optical band gap of the crystal was determined from the UV Visible NIR absorbance spectrum and found to be 3.18 eV. The electronic polarisability of the grown crystal was calculated from the band gap. The nature of the spectrum shows its potential as an NLO material. Thermal properties and thermal stability were studied by conducting Thermo-gravimetric and Differential Thermal Analysis. Here the melting point was observed as 49.5 degree Celsius which is well matching with the theoretical value. It is also thermally stable up to 150 degree Celsius.**

Keywords—Benzophenone, gel growth, Single crystal Xray diffraction, FTIR, UV-Vis-NIR spectral analysis, Thermal analysis

I. INTRODUCTION

Crystals play an inevitable role in modern technology. So crystal growth is a prominent area in the scientific and technological research. Since the crystal growth has immense applications, it is an interdisciplinary subject covering physics, chemistry, materials science, chemical engineering, metallurgy, crystallography, mineralogy etc. There is growing interest on crystal growth to meet the demand of materials for technological applications [1].

The growth of NLO materials has become trend in recent years. They are having technological importance in the field of optoelectronics, lasers, data storage systems and optical communication [2]. These materials should possess large second order optical non linearities, short transparency, cut off wavelength and thermal stability [3]. NLO response is larger in organic materials when compared to inorganic materials due to the presence of active π bonds [4]. So we focus our studies on organic materials.

Benzophenone is one of the most important organic materials showing NLO property [5]. It is an important compound in organic photochemistry and perfumery as well as in organic synthesis. It is also used as a photo-initiator of UV curing applications in inks, adhesive and coatings, optical fiber as well as in printed circuit boards[5]. Rapid crystal growth of benzophenone by low temperature solution growth and unidirectional seeded single crystal growth from solution of benzophenone [5, 6] has already been reported.

Here we have grown benzophenone crystals by gel method to improve the quality of the crystals. The gel growth is simple in technique, effective in growing single crystals of compounds that cannot be easily grown by other methods [7]. In this paper, we are presenting the XRD characterization and spectral and thermal studies of gel grown benzophenone crystals.

II. EXPERIMENTAL - GROWTH OF SINGLE CRYSTALS

Single crystals of benzophenone were formed by gel diffusion technique. The technique involves the setting of gel and addition of required top solution over the set gel. The crystallization apparatus for the growth consists of borosilicate glass test tube of length 20 cm and diameter 2.5 cm placed vertically on a stand. The solution for gel having specific gravity 1.03-1.05 was prepared by dissolving sodium meta silicate (SMS) in double distilled water. The solution was then acidified with 1M glacial acetic acid to get the pH in the range 4 - 7(in steps of 0.5) and taken about 30 ml of each in different test tubes. They were kept undisturbed for gel setting. Over the set gel, the top solution prepared by dissolving AR grade benzophenone in ethanol was added drop wise through the side of the test tube to prevent the gel breakage. The test tubes were covered with transparent plastic sheets to avoid evaporation and contamination of solution. The crystals were found growing over the gel surface within 1 day and the growth lasted for about 50 days. It is also found that pH = 6 and gel density 1.04 g/cc was the optimum condition for the growth of best quality benzophenone crystals.

III. RESULTS AND DISCUSSIONS

A. Single crystal X-ray diffraction

The crystallographic data of gel grown benzophenone crystal were obtained by using Bruker Kappa Apex II X ray diffractometer and is shown in table I.

TABLE I

Unit cell parameters	**a = 7.968A^0** **b = 10.304 A^0** **c = 12.098 A^0** **α = β = γ = 90^0**
Volume	**993.2 (A^0)^3**
Lattice type	**Orthorhombic P**

The valence electron plasma energy, $\hbar\omega_p$ is given by

$$\hbar\omega_p = 28.8\left(\frac{Z\rho}{M}\right)^{\frac{1}{2}} \quad (1)$$

where Z is the total number of valence electrons, ρ is the density of the crystal, M is the molecular mass of the crystal[8].

The Fermi Energy E_F can be calculated using the formula [8]

$$E_F = 0.2948(\hbar\omega_p)^{\frac{4}{3}} \quad (2)$$

For the grown crystal, we have Z = 68, ρ = 1.2185 g/cc and M = 182.2179 g/mol. The calculated values of valence electron plasma energy and Fermi energy of benzophenone crystal are 19.42 eV and 15.39 eV respectively.

B. Fourier Transform Infrared Spectroscopic Studies (FTIR)

The FTIR spectrum of gel grown benzophenone crystal is shown in the *Fig. 1*.

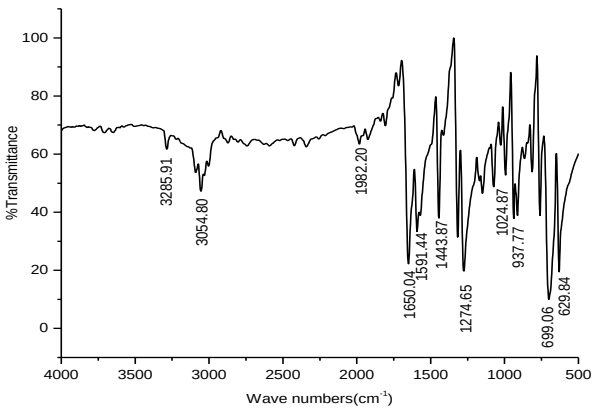

Fig. 1. FTIR spectrum of Benzophenone crystal

In the higher wavelength region, the peak at 3054.80 cm^{-1} is associated with aromatic C-H stretching. The peak at 1650 cm^{-1} represents C=O stretching. The skeletal vibrations are represented by the peaks 1591.44 cm^{-1} and 1443.87cm^{-1}. The region between 1274.65 and 1024.87 cm^{-1} represents the in plane bending modes of C-H while the peaks below 1000 cm^{-1} represents out of plane bending modes.

C. UV-Vis NIR spectral analysis

The UV-visible absorption spectrum of benzophenone crystal shown in *Fig. 2* was recorded in the range 214 nm to 1200 nm using the instrument Varian Cary 5000 UV Vis NIR spectrometer.

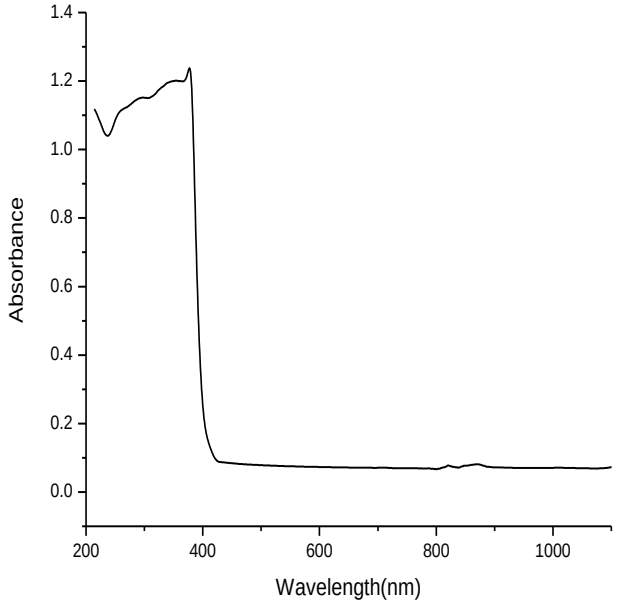

Fig. 2. UV visible spectrum of Benzophenone crystal

The transmission range and cut off wavelength of the crystals are very crucial in many important practical applications. Here a strong absorption is taking place at 377 nm, which is the lower cut off wavelength. There is no significant absorption in the visible range. This transparent region makes the benzophenone crystal suitable for optoelectronic applications [9, 10].

The optical band gap E_g can be calculated from the absorption spectrum using the equation

$$(\alpha h\nu)^n = A(E_g - h\nu) \quad (3)$$

where A is a constant, E_g is the optical band gap, h Planck's constant and ν frequency of the incident photons, α absorption coefficient[11].

Fig. 3 shows a graph drawn between $(\alpha h\nu)^3$ versus hν . E_g is calculated as 3.18 eV by extrapolating the linear part of the graph.

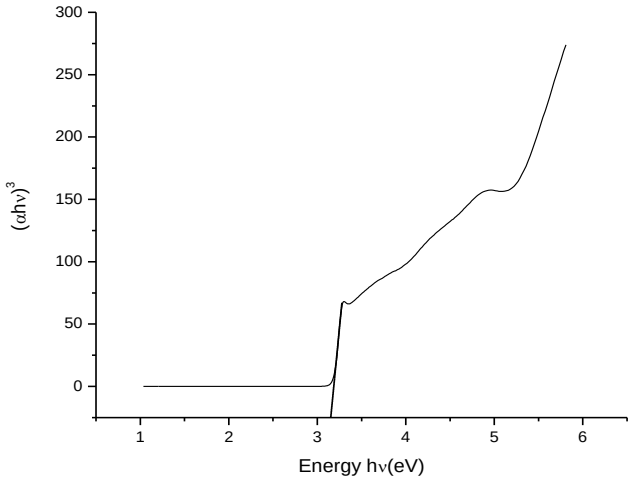

Fig. 3. Plot of $(\alpha h\nu)^3$ versus photon energy

The electronic polarisability of the crystal can be calculated from the band gap using the equation [12]

$$\alpha = \left[1 - \frac{\sqrt{E_g}}{4.06}\right] \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^3 \qquad (4)$$

and its value is found to be $3.32 \times 10^{-23} cm^3$.

D. Thermal Analysis

Thermo-gravimetric analysis (TGA) and Differential thermal analysis (DTA) were carried out for thermal studies. TGA and DTA curves are shown in *Fig. 4.*

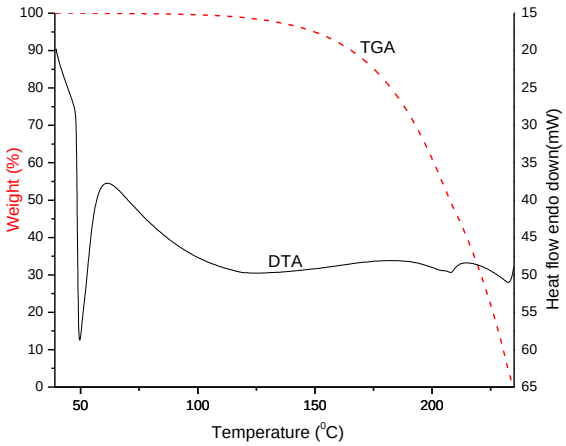

Fig. 4. TGA/DTA curves of Benzophenone crystal

In the DTA graph, the endothermic peak at 49.55^0C corresponds to the melting point of the crystal. Here the melting point is found to be more than the melting point of benzophenone crystals grown by other method (41.36^0C) [6].The sharpness of the endothermic curve shows good degree of crystallinity. The TGA graph shows that the crystal is thermally stable up to 150^0C.

IV. CONCLUSION

Good quality benzophenone crystals were grown by gel diffusion technique with optimum conditions of gel density 1.04 g/cc and pH value 6. The valence electron plasma energy and Fermi energy was calculated as 19.42 eV and 15.39 eV respectively from the crystallographic data obtained by single crystal XRD technique. FTIR spectrum has revealed the vibrational modes which identifies the grown crystal. The optical band gap of the crystal was determined as 3.18 eV from the UV visible spectrum. The electronic polarisability of the crystal was also calculated from the band gap .The crystal is having a transparent region which makes it suitable for NLO applications. The crystal is thermally stable up to 150^0C and the melting point was determined as 49.55^0C.

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