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Archives of Applied Science Research, 2012, 4 (2):898-905  
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## Rapid crystal growth of benzophenone by low temperature solution growth and its characterization

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### ABSTRACT

Low temperature solution growth (LTSG) is one of the most efficient and simplest processes which can be employed for crystal growth from solutions. The ease in handling and the readiness in its miscibility with the solvents make it an attractive technique for crystal growth. Most of the chosen solutes are miscible with water and some are with alcohol and ethers. Benzophenone a photoinitiator used in the UV-curing applications in inks, adhesive and coatings, optical fibers and in printed circuit boards. Benzophenone or di-phenyl ketone (CAS No. 119-61-9) with chemical formula  $(C_6H_5)_2CO$  is miscible with ethanol in optimal proportions. The solution is heated for supersaturation well below its boiling point. The supersaturated solution is then taken in a beaker and kept for crystallization. Normal nucleation followed by crystallization happens by evaporation technique at room temperature. A provision for rapid evaporation by a stream of uniform hot air flow across the growth chamber enhances the crystallization rate thereby reducing the time required for the growth of crystals. This acceleration of crystal growth is an important prerequisite for the mass crystallization and industrial crystal growth. The crystals are analysed for their surface, structural and spectroscopic characteristics.

**Keywords:** Benzophenone, photoinitiator, ultra-violet filter, Nonlinear optic, Absorption, Transmission, FTIR

### INTRODUCTION

Benzophenone, an aromatic ketone (diphenyl ketone), is an important compound in organic photochemistry and perfumery as well as in organic synthesis. It is a white crystalline substance with rose-like odor; insoluble in water; melting point  $49^\circ\text{C}$ ; boiling point  $305 - 306^\circ\text{C}$ . Benzophenone is used as a constituent of synthetic perfumes and as a starting material for the manufacture of dyes, pesticides and drugs (especially anxiolytic and hypnotic drugs). Benzophenone is used as a photoinitiator of UV-curing applications in inks, adhesive and coatings, optical fiber as well as in printed circuit boards. Photoinitiators are compounds that break down into free radicals upon exposure to ultraviolet radiation. Photoinitiators undergo a unimolecular bond cleavage upon irradiation to yield free radicals (benzoin esters; benzil ketals; alpha-dialkoxy acetophenones; alpha-hydroxy alkylphenones; alpha-amino alkylphosphine; acylphosphine oxides). Another type of photoinitiators undergo a bimolecular reaction where the excited state of the photoinitiator interacts with a second molecule (a co-initiator) to generate free radicals (benzophenones, amines; thioxanthenes,

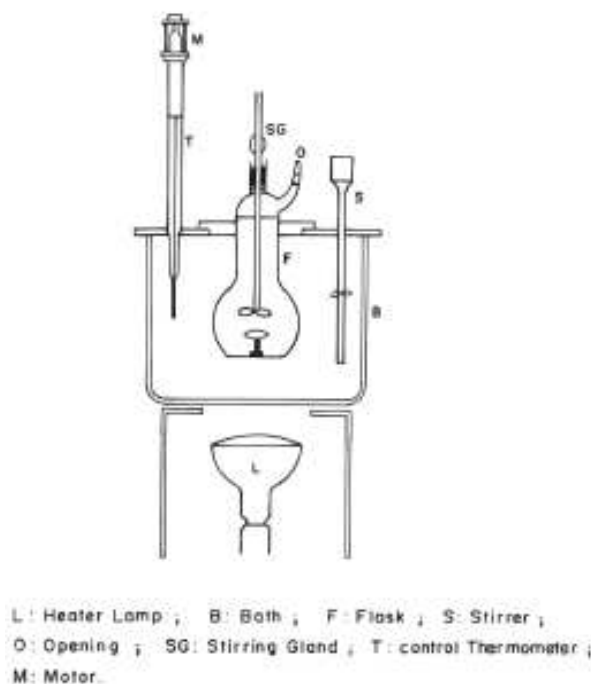


titanocenes). Ultraviolet radiation has more energy than visible light, and thus degrade the physical properties such as the appearance of organic substances and plastics. Benzophenones can act as optical filters or deactivate substrate molecules that have been excited by light for the protection polymers and organic substances. Their, cosmetic grades, are used as sunscreen agents to reduce skin damage by blocking UV. Benzophenone is a promising NLO material where the absorption is visible in the blue light region having a cut-off wavelength lower than 450nm [1,2,3].

### MATERIALS AND METHODS

Growth of crystals from aqueous solutions is one of the ancient methods of crystal growth. The method of crystal growth from low temperature aqueous solutions is extremely popular in the production of many technologically important crystals. It is the most widely used method for the growth of single crystals. The growth of crystals by low temperature solution growth involves weeks, months and sometimes years. Though the technology of growth of crystals from solution has been well perfected, it involves meticulous work, much patience and even a little amount of luck. A power failure or a contaminated batch of raw material can destroy months of work.

**Fig 1: Solution Growth Apparatus**



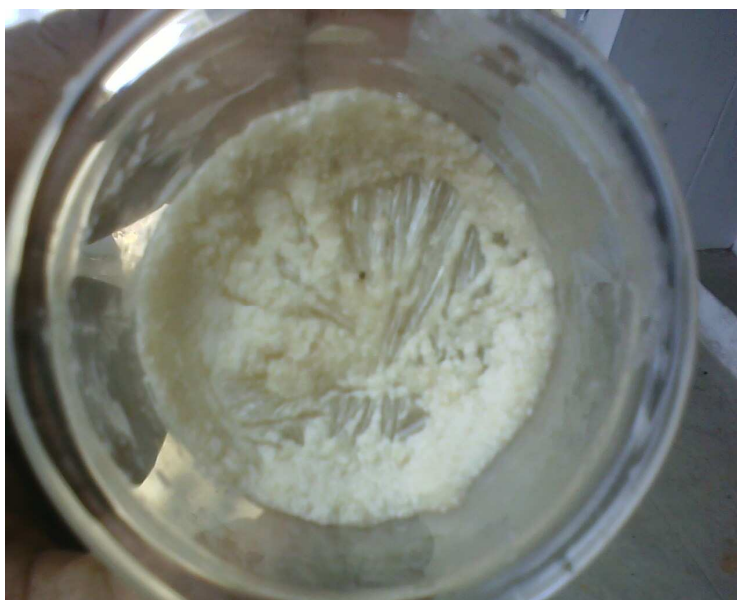
Materials having moderate to high solubility in a particular temperature range, ambient to 100 °C at atmospheric pressure can be grown by low-temperature solution method (James and Kell 1975). The mechanism of crystallization from solutions is governed, in addition to other factors, by the interaction of ions or molecules of the solute and the solvent which is based on the solubility of substance on the thermodynamical parameters of the process; temperature, pressure and solvent concentration (Chernov 1984). The advantages of crystal growth from low temperature solution nearer the ambient temperature results in the simple and straight forward equipment design which gives a good degree of control of accuracy of  $\pm 0.01$  °C. Due to the precise temperature control, supersaturation can be very accurately controlled. Also efficient stirring of solutions reduces fluctuations to a minimum. The low temperature solution growth technique is well suited to those materials which suffer from decomposition in the melt or in the solid at high temperatures and which undergo structural transformations while cooling from the melting point and as a matter of fact numerous organic and inorganic materials which fall in this category can be crystallized using this technique The low temperature solution growth technique also allows variety of different morphologies and polymorphic forms of the same substance can be grown by variations of growth

conditions or of solvent (Hooper et al 1979). The proximity to ambient temperature reduces the possibility of major thermal shock to the crystal both during growth and removal from the apparatus.

Benzophenone is taken as a solid flaky salt and dissolved in ample amount of alcohol till it reaches saturation state. Then the solution is heated gently in order to obtain the supersaturated state beyond which the salt becomes insoluble in the solvent viz., alcohol. The solubility and supersolubility of Benzophenone was observed to be 10 grams and 15 grams per 100ml of ethanol solvent. Then the supersaturated solution is then filtered using Schott Duran Filter paper (pore size 5 micron) and left inside the constant temperature solution growth process for nucleation and subsequent crystallization. The nucleation time was measured for repeatability and was observed to be 452 seconds.



**Fig 2: Cleaved Crystal of Benzophenone**



**Fig 3. Top view of the as-grown crystal with froth in the beaker**

The solution was left for crystallization in a constant temperature water bath where the ambient temperature of the bath was optimally kept at 35°C for complete solute utilization where the solvent was found to evaporate fully forming Benzophenone Crystals in the beaker in which it was kept to grow.

As grown crystals of Benzophenone were cleaved and presented for observation. A cleaved sample of size 4.5 cm x 4.5 cm x 4 cm was the largest crystal out of the sample rapidly crystallized using solution growth apparatus.

#### Microindentation Tests

Among the various method of hardness measurements, the most common and reliable method is the Vicker's hardness test method. It was done using a Leitz Wetzlar Microhardness tester and observed using a Metallux microscope. In this method, microindentation is made on the surface with the help of a diamond pyramidal indenter. Smith and Sandland have proposed that a pyramid be substituted for a ball in order to provide geometrical similitude under different values of load. The Vicker's pyramid indenter where opposite faces contain an angle ( $\alpha = 136^\circ$ ) is the most widely accepted pyramid indenter. Pyramid indenters are said to be best suited for hardness tests due to two reasons namely

- i. The contact pressure for a pyramid indenter is independent of indent size.
- ii. Pyramid indenters are less affected by elastic release than other indentors.

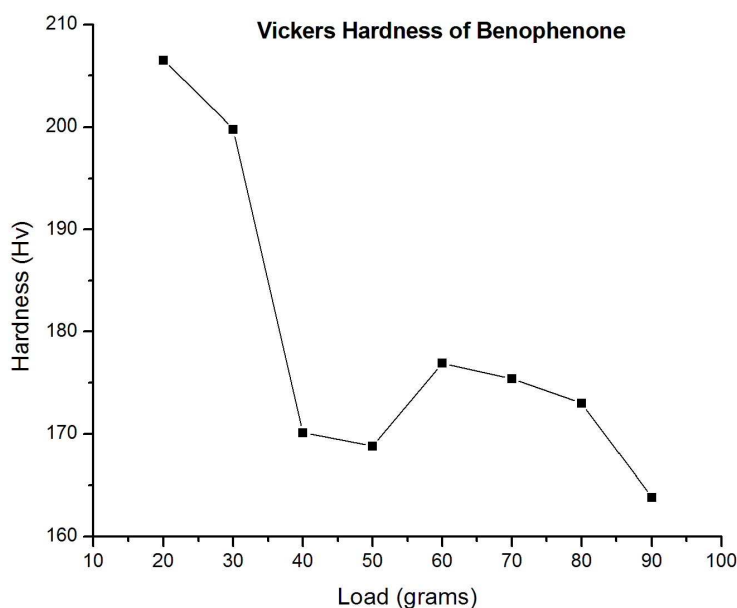
The base of the Vicker's pyramid is a square and the depth of indentation corresponds to 1/7<sup>th</sup> of the indentation diagonal. The Vicker's hardness number  $H_v$  or Diamond Pyramid Number (DPN) is defined as.

$$H_v = \frac{2W \sin \alpha / 2}{d^2}$$

Where  $\alpha$  is the apex angle of the indenter ( $\alpha = 136^\circ$ ). The Vicker's hardness number is therefore calculated from the relation

$$H_v = \frac{W}{\text{Pyramid area}} = \frac{1.8544 \times W}{d^2} \text{ kg/mm}^2$$

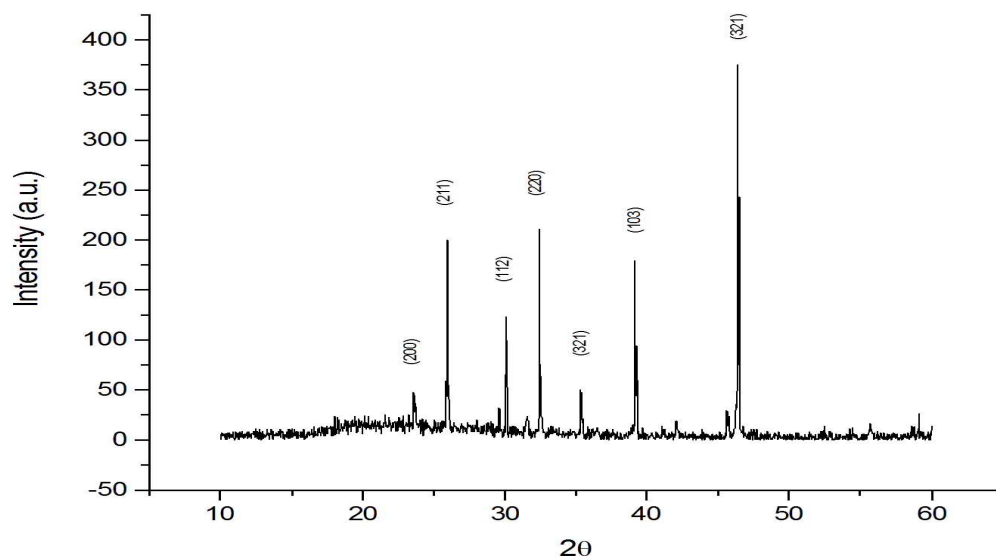
Benzophenone crystal had a maximum Vickers microhardness value of 206 for 20grams and a minimum of 162 for 90 grams load.



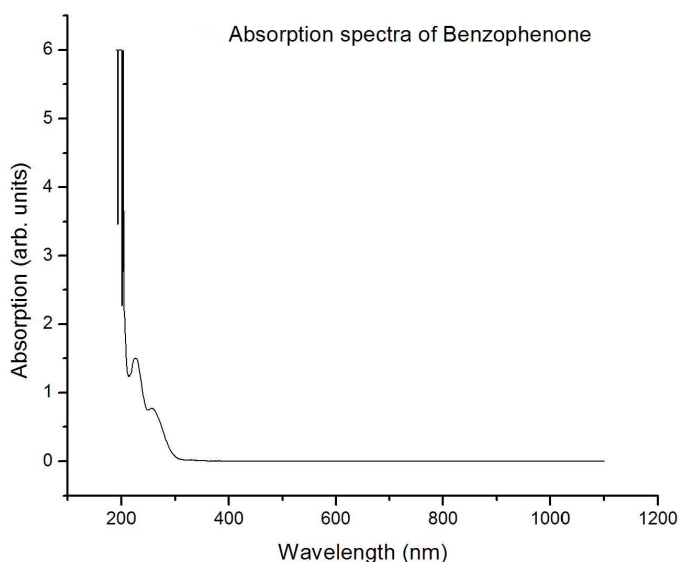
**Fig.4 Vickers Microhardness tests for Benzophenone**

**XRD-ANALYSIS**

Powder X-Ray diffraction was carried out with the as grown crystals in powdered form. The powdered samples were loaded into a Rigaku X-ray diffraction apparatus using CuK $\alpha$  radiations having  $\lambda=1.5045 \text{ \AA}$  and analysed for confirmation. The crystallographic data of the lattice parameters [4] obtained were  $a=9.751 \text{ \AA}$ ,  $b=10.671 \text{ \AA}$ ,  $c=24.813 \text{ \AA}$ ,  $\alpha=87.47$ ,  $\beta=83.80$ ,  $\gamma=63.154$ . Benzophenone exhibited as a face centered monoclinic structure with space group C and volume of the unit cell was  $V=2290.46 \text{ \AA}^3$ . The results were compared with the ICDD database files and conformed with four of the available peak values (200), (220), (103) and (321)



**Fig.5: Powder XRD of Benzophenone**

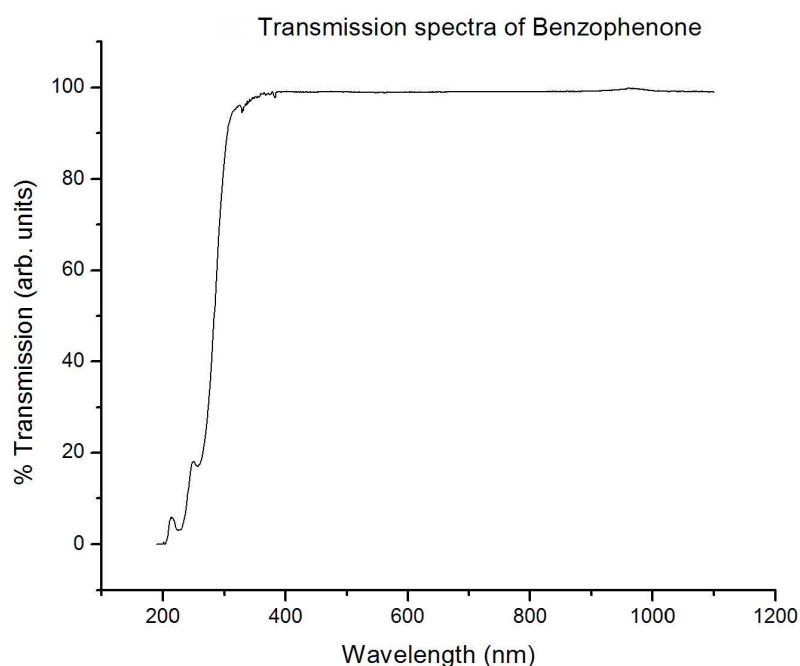


**Fig.6: UV-VIS Absorption Spectra of Benzophenone**

**UV-VIS spectroscopic analysis**

The Absorption spectra of Benzophenone was taken in a Lambda 35 UV-VIS spectrophotometer where two prominent absorption maxima were observed at 225nm and 255nm respectively. It also has two additional maxima, one at 285nm and another at 345nm. It is observed that Benzophenone gives some UVB protection but is particularly useful in the UVA region, the region that is the principle cause of colour loss and perfume degradation.

A transmission peak at 255nm signifies a  $\pi$  to  $\pi^*$  transition and identification of the presence of the benzene rings in the radical. Aromatic systems, which contain p electrons, absorb strongly in the ultraviolet. This is evident by a previous transmission peak at 245nm. Two more prominent peaks were observed at 328nm and 382 nm of the transmission spectra in addition to the 225nm and 255nm peaks observed earlier.



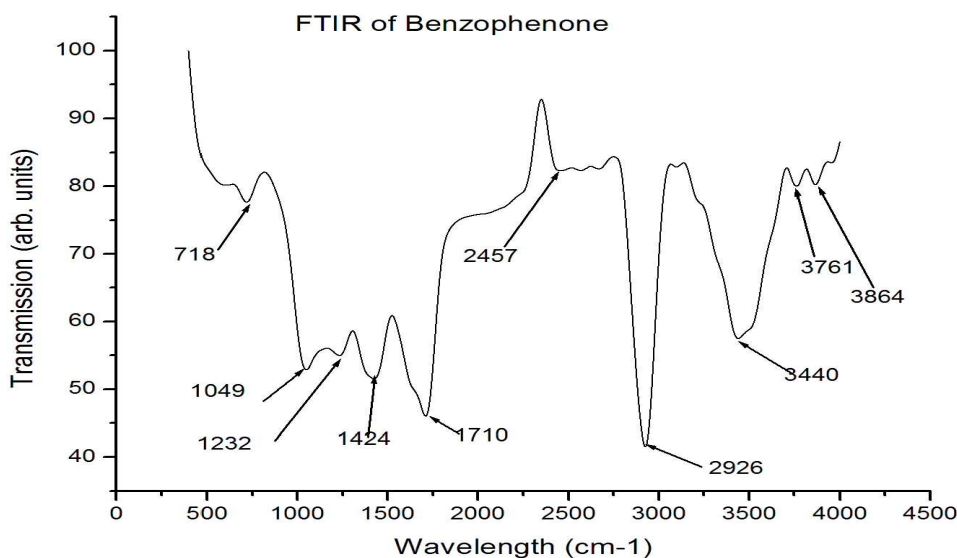
**Fig.7. Transmission Spectra of Benzophenone**

**Fourier transform iinfra-red analysis**

The existence of one or more aromatic rings in a structure is normally readily determined from the C-H and C=C-C ring-related vibrations. The C-H stretching occurs above  $3000\text{ cm}^{-1}$  and is typically exhibited as a multiplicity of weak-to-moderate bands, compared with the aliphatic C-H stretch. The structure of the bands is defined by the number and positions of the C-H bonds around the ring, which in turn are related to the nature and number of other substituents on the ring. The other most important set of bands are the aromatic ring vibrations centered around  $1600$  and  $1500\text{ cm}^{-1}$ , which usually appear as a pair of band structures, often with some splitting. The appearance and ratio of these band structures is strongly dependent on the position and nature of substituents on the ring.

For simple aromatic compounds, a series of weak absorptions may be observed between  $2000$  and  $1700\text{ cm}^{-1}$ . These are multiple combination bands that are noticeably weak, and are typically not to be confused with an isolated weak carbonyl absorption. The C-H bending vibrations can also be used to support the presence of an aromatic structure. If there are medium-to-strong absorptions, sometimes more than one, between  $850$  and  $670\text{ cm}^{-1}$ , these can be assigned to C-H out-of-plane bending on an aromatic ring. These support the assignment of the  $1600/1500\text{ cm}^{-1}$  bands, and the locations of the bands are often indicative of the nature of the substitution of the aromatic ring. For simple structures, it is possible to differentiate mono-, di- (ortho, meta and para), and certain poly-substitutions. Note that a single, strong band may support simple ortho (around  $750\text{ cm}^{-1}$ ) or para (around  $830\text{ cm}^{-1}$ ) substitution.

Many organic compounds have multiple band structures in the region 1150–950  $\text{cm}^{-1}$ . The in-plane C-H bending vibrations of aromatic compounds typically occur in this region, and can exist as complex band structures (multiple, well-defined bands). They tend not to be diagnostic for many compounds because of conflict and overlap with other functional group absorptions, including some skeletal (backbone) vibrations.



**Fig.8: FTIR spectra of Benzophenone**

The FTIR spectrum was analysed using a BRUKER Spectrometer using a KBr pellet in the range 4000 to 400  $\text{cm}^{-1}$  shown in fig.8. In Benzophenone crystal, asymmetric and symmetric stretching vibrations were observed at 3864  $\text{cm}^{-1}$  and 3761  $\text{cm}^{-1}$  respectively. The aromatic stretching vibrations appear around 3440  $\text{cm}^{-1}$ . A well defined peak is observed at 1710  $\text{cm}^{-1}$  which is due to C=O stretching vibration of the carbonyl group. The presence of C=C aromatic ring vibrations are evident at 1232  $\text{cm}^{-1}$  and 1424  $\text{cm}^{-1}$ . The group peaks between 1049  $\text{cm}^{-1}$  and 718  $\text{cm}^{-1}$  are due to the aromatic CH bends.

#### **Conversion efficiency**

The conversion efficiency of the crystal was checked using the powder SHG technique developed by Kurtz and Perry. The crystal was ground into powder and densely packed in between two glass slides. An Nd:YAG laser beam of wavelength 1064 nm was made to fall normally on the sample cell. The emission of green light confirms the second harmonic generation of Benzophenone which was qualitatively higher in intensity to the reference KDP and ADP crystals provided.

#### **CONCLUSION**

Crystals of Benzophenone were grown rapidly by low temperature solution growth technique at room temperature. The structural, optical and qualitative NLO efficiency properties were analysed. The microhardness values were found to be higher than reported values [5]. The UV-VIS spectra recorded a near 95% transparency for the cleaved samples of Benzophenone along the (001) orientation. The FTIR analysis proves that the assignments were in order for Benzophenone depicting aromatic consistency and confirmatory in individual band assignments.

#### **Acknowledgement**

One of the authors A.C wish to thank Prof. P. Ramasamy, Dean-Research, SSNCE, Kalavakkam, Dr. N.Vijayan and Dr. G.Bagavannarayana of National Physical Laboratory, New Delhi and Dr.V.Vaithianathan of Chonnam National University, Gwanju, South Korea for extending many characterization facilities. The Authors are also thankful to

Dr. P.K.Baskaran, Principal and Prof. A. Poyyamozhi, HOD, Dr. K.B. Rajesh, Assistant Professor, PG Department of Physics, Govt. Arts College, Dharmapuri for constant encouragement and support.

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