

Synthesis, growth, spectral, optical, thermal, dielectric and nonlinear optical studies of new aryldiene crystal: 2, 6-Difurfurylidene cyclohexanone

S.Sathiamurthi^{1*} and P.Srinivasan²

¹Department of Physics, Sairam Institute of Technology, Chennai

²University College of Engineering, Panruti, 607106

*Corresponding author: E-Mail: sril35@gmail.com

ABSTRACT

Single crystal of 2, 6-Difurfurylidene cyclohexanone (DFCH) was synthesized by Claisen–Schmidt condensation reaction and grown by slow evaporation yields the organic crystals of size 15x4x1 mm³. The functional groups were identified by Fourier Transform Infra-Red (FTIR) and Fourier Transform Raman spectral analysis. Optical transparency region and lower cutoff wavelength were analysed by UV-vis-NIR studies. Thermal stability and decomposition temperature were calculated by using Thermo gravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC). The dielectric properties of DFCH from 313 to 393k were studied by the impedance analysis. The powder test with Nd:YAG laser radiation provides the second harmonic generation.

KEY WORDS: dielectric, nonlinear, optical.

1. INTRODUCTION

At present, design of organic NLO materials are superior than its counterpart inorganic materials, because of the advantages of large nonlinearity, easy synthesis, having variety of donor and acceptor substituents, good transparency over visible region and good thermal stability made the material for the applications of optical switches, modulators, optical limiters and optical data storage. Hyper polarizability in these compounds is due to the conjugated system which has electronic origin make the response is ultrafast. Charge transfer through the conjugated system could be enhanced by substituting the donor and acceptor substituents to enhance the hyper polarizability. In Poly phenyls theoretical calculation shows that the maximum macroscopic nonlinear response is reached for two or three ring systems. In recent years, chalcones with two aromatic rings were studied in large number. As part of our investigation of organic NLO material, we synthesised the new aryldiene compound 2, 6-bis (difurfurylidene) cyclohexanone (DFCH) which has two furfural rings joined by a cyclohexanone ring.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis: The title compound was synthesized by the Claisen–Schmidt condensation reaction. Claisen–Schmidt condensation reaction is the reaction of a substituted benzaldehyde with substituted acetophenone in the presence of an alkali, as a catalyst. The title compound DFCH was synthesized by stirring cyclohexanone and furfuraldehyde in methanol at room temperature. NaOH dissolved in water was added drop wise and the mixture was stirred for 4 hours. Then the mixture was poured into the ice cold water. Two drops of HCl was added to neutralize the alkali. The crude product was filtered and washed with water many times. By slow evaporation method, the DFCH dissolved in acetone was kept in a beaker for two months yield the crystals of size 15x4x1 mm³. Synthetic scheme for the title compound is given in Fig.1. Also the crystal photograph is shown in Fig.2.

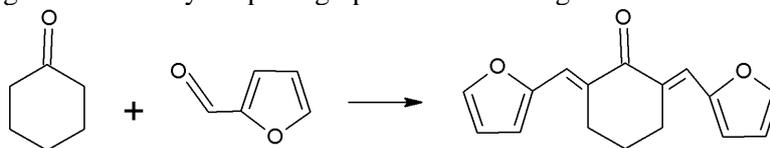


Figure.1.Synthesis of DFCH



Fig.2.Photograph of DFCH

3. RESULTS AND DISCUSSION

3.1. Fourier transform Infrared (FT-IR) and Fourier transform Raman spectral analysis: FT-IR and FT-Raman spectrum were carried out to identify the functional groups and their vibrational modes. In order to obtain FTIR spectrum, the sample was prepared by mixing the compound with KBr pellets. The spectrum was recorded between 400 and 4000 cm^{-1} using a JASCO 6300 FT-IR spectrometer equipped with a KBr beam splitter and a DTGS detector, with a spectral resolution of 1.92847cm^{-1} . The FT-Raman spectrum was recorded using a BRUKER RFS 27, Standalone FT-Raman Spectrometer, having spectral resolution of 2cm^{-1} with an exciting wavelength of 1064nm from an Nd:YAG laser source. FT-IR and FT Raman spectra are given in Fig.3 and Fig.4. The existence of bonds with different dipole moment in the DFCH molecule is identified by the difference in strength of the absorbance of peaks. The shift in frequency shows the different energy requirement for the molecule for absorbing infrared radiation. The peak assignments of functional groups are tabulated in Table 1. The vibrational bands confirmed the structure.

Table.1. Functional groups assignment.

Wave number cm^{-1}		Assignments
FT-IR	FT Raman	
3145.33		Aromatic C-H stretching vibration
	1645.6	C=O stretching vibration
1548.52	1590.35	Aromatic ring variations
1259	1477.51	Aromatic in plane bending vibrations
1276.65	1164.6	C-O structure
739	720.5	Out of plane, C-H bending

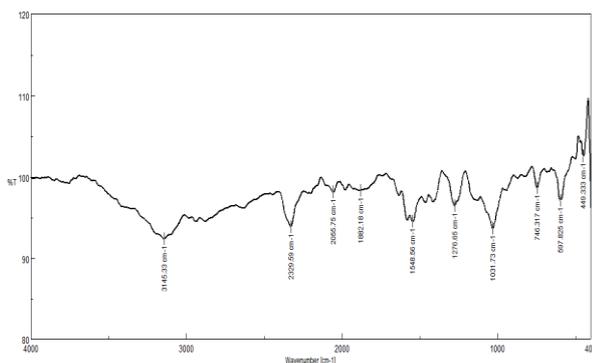


Fig.3. FTIR spectrum of DFCH

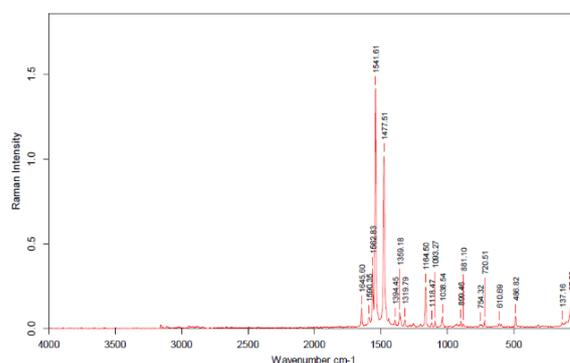


Fig.4. FT Raman Spectrum of DFCH

3.2. Thermal Studies: The thermal stability and melting point were calculated using Perkin Elmer 524A3112802 simultaneous TGA and DSC analyser. The analysis is done with a sample of 9.11 mg in the temperature difference of 27-400 $^{\circ}\text{C}$, at a rate of 5 $^{\circ}\text{C}/\text{min}$, in argon gas atmosphere. The TGA and DSC analysis is shown in Fig 5.

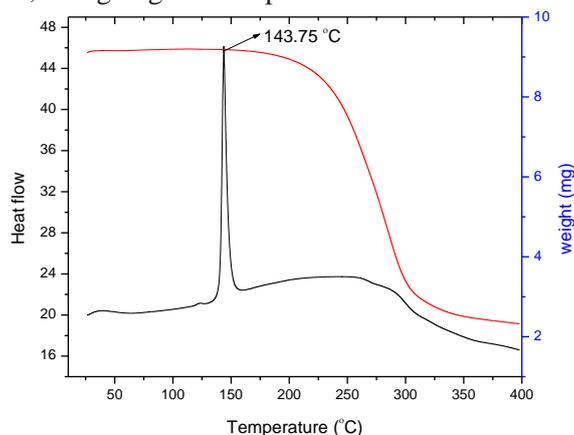


Fig.5. DSC and TGA of DFCH

The sharp peak at 143.75°C corresponds to the melting point of DFCH. It is in well agreement with the capillary tube melting point method. The sharpness indicates the purity and good crystalline nature of the sample. From the TGA curve, decomposition starts from the melting point and 70% of decomposition taken place up to 326.65°C . Decomposition may be due to conversion of gaseous products. DFCH has comparably high melting point when compare to other chalcone crystals. It is thermally stable upto the melting point may favour the sample for the device fabrication.

3.3. UV-Visible-IR spectral studies: Optical transparency at visible and near visible frequency regions are pre requirement for the good NLO crystal. If absorption takes place in these region or its harmonics may affect the conversion efficiency. UV-vis-NIR absorption spectrum of the crystal was recorded using a Shimadzu- UV 2600 UV-vis spectrophotometer in the wavelength range of 200–1200 nm. A solution of DFCH in acetone was placed in a 1cm thick cuvette for measurement. The recorded absorption and calculated transmittance spectrum are shown in Fig. 6. As shown in the figure, the crystal has less absorption in the visible region of the spectrum. The peak absorption observed in the curve can be assigned to the $n-\pi^*$ transition and may be attributed to the excitation of the aromatic ring and C = O group of the molecule. From Fig. 6, it is clear that maximum absorption is centered at 459 nm and this wavelength corresponds to the cut-off wave-length of the crystal beyond which there are no significant absorption peaks till IR region. The longer cut off wave length may be due to furfural rings rather than benzene rings. Wider transparency region in DFCH may be the advantage for making the optical devices. The absorption values are calculated from the transmission values and the Tauc plot was drawn between $(\alpha h\nu)^2$ and $h\nu$. The optical band gap was calculated by extrapolating from the linear portion of the graph to the energy axis and the optical band gap for the direct band material is found to be 2.06 eV, from Fig 7.

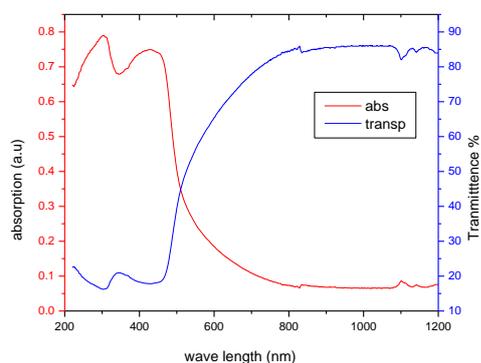


Fig.6. Absorption and transmission spectrum of DFCH

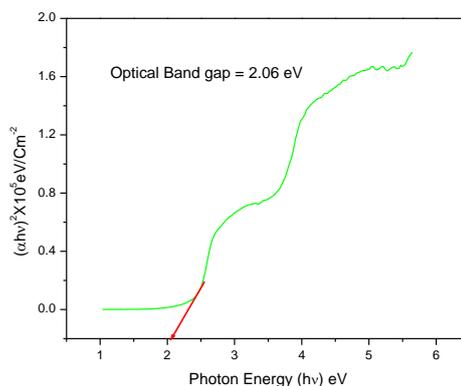


Fig.7. Calculation of optical band gap of DFCH

3.4. Dielectric studies: Dielectric measurements were carried by KEITHLEY model 6517A. The capacitance and dielectric loss factor ($\tan\delta$) measurements were carried out to an accuracy of +2% using an LCR meter with five different frequencies, viz. 100Hz, 1 kHz, 10kHz and 100 kHz at various temperatures ranging from 40 – 120°C. The graph of the dielectric loss factor $\tan \delta$ and the dielectric constant ϵ_r and at various frequencies for the crystal plate of DFCH is shown in Fig 8 and Fig.9 respectively. The graphs show that ϵ_r and $\tan \delta$ values were not varying much with higher frequencies. Also the dielectric loss factor is very low, except at low frequencies. Grain boundaries and defects may be the cause for the slight higher values of ϵ_r and $\tan \delta$ at low frequencies

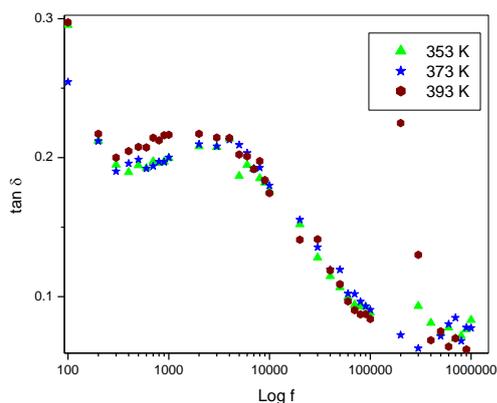


Fig.8. Variation of dielectric loss with variation in frequency

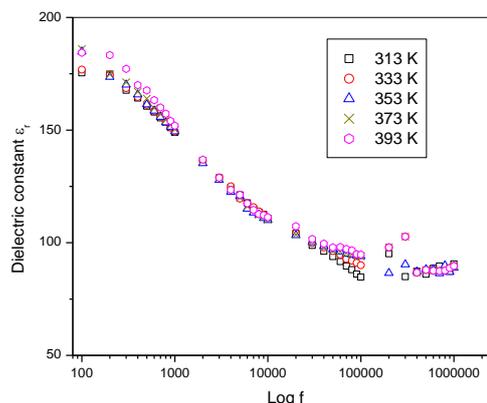


Fig.9. Variation of dielectric constant with variation in frequency

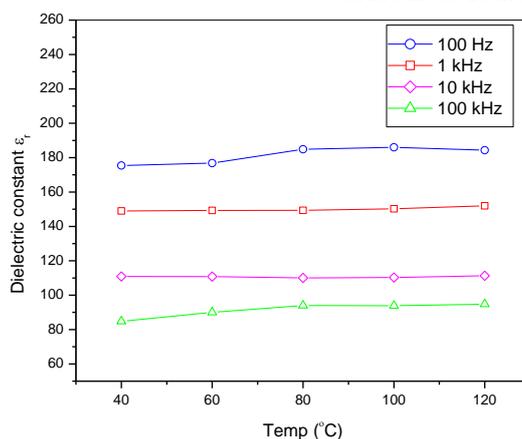


Fig.10.Variation of dielectric constant with temperature for specific frequencies

3.5. Nonlinear optical studies: Second harmonic test was carried on the BBCH using Kurtz-Perry method. The input laser beam was passed through IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of diameter 0.154 mm. For the SHG efficiency measurements, microcrystalline material of KDP and Urea were used for comparison. When a laser input of 0.68 J was passed, it has given the output of 1.2 mJ. It has the relative efficiencies of 13.63% and 13.48% with KDP and Urea respectively.

4. CONCLUSION

The nonlinear optic crystal BBCH was synthesized by slow evaporation technique. The functional groups were identified by FTIR and FT-Raman analysis. The UV-Vis-IR studies shows that the BBCH has the transparency range from 459 nm to the IR region. The melting point of 143.75°C is confirmed by the TGA-DSC and also by melting point method. Dielectric measurement studies proves that the BBCH has low dielectric loss and low dielectric constant. Transparency in visible and IR region, low dielectric loss and low dielectric constant and comparably high melting point among organic crystal may favour the BBCH for optical device fabrication.

5. ACKNOWLEDGEMENT

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