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Studies on linear and nonlinear optical properties of 2-{[2-Trifluoromethyl)phenyl](hydroxy) methyl} cyclododecanone crystal

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Abstract: 2-{[2-(Trifluoromethyl) phenyl] (hydroxy) methyl}cyclododecanone (2CF3-CDD) has been synthesized by direct aldol condensation reaction. The crystals weregrown in the mixture of solvent tetrahydrofuranand ethanol by slow evaporation method.The linear optical property of the crystal has been studied using UV-VIS-NIR spectroscopy. The optical constants are calculated theoretically in the wavelength range 190-1100nm. The third order nonlinear optical property of the crystal has been investigated by using z-scan technique with He-Ne laser (632.8nm). The saturation absorption and self-defocusing effect was observed in z-scan open and closed aperture methods respectively. The response time of the crystal has found to be in the order of milliseconds.The two figures of merit W>1andT<1 are suitable for optical switching application. The refractive index of the crystal has been measured using Abbe's refractometer and it is found to be 1.609.
Keywords: Studies on linear and nonlinear optical properties of 2-{[2-Trifluoromethyl)phenyl] (hydroxy) methyl} cyclododecanone crystal.

1. Introduction

In several areas of optoelectronics have been a huge interest for organic materials because the possibilities of optimization of this nonlinearity through manipulation of their composition[1]. Organic compounds are optically more nonlinear than inorganic materials because of their hydrogen bonds and weak Vander Waal's and it possess a high degree of delocalization [2]. The direct aldol condensation of benzaldehyde to cyclododecanone (CDD) reactions forms β-hydroxy carbonyl compounds and monobenzylidenecyclodo decanone derivatives. The β–carbonyl compounds were stabilized by hydrogen bond interaction between the –OH group and –C=O groups. The monobenzylidene derivatives are due to less stable hydrogen bonds between –OH and –C=O groups, electrostatic interaction between aldehyde substituents and metal forms C–H···O molecular interaction [3]. In the present investigation, systematic studies on the synthesis, growth, NMR, optical and third order susceptibility of the compound is investigated by Z-scan method.

2. Experimental

The molecular ratio(1:1) of reactants cyclododecanone and 2-trifluoro benzaldehyde were completely dissolved in methanol in the presence of sodium hydroxide as catalyst. The mixture was stirred well for the direct aldol condensation reaction about 3 hours at room temperature, to synthesize the β-hydroxy carbonyl

compounds and monobenzylidenecyclododecanone derivatives [3].2CF3-CDD crystal is shown in Fig[1].The chemical structure of the synthesized compound was confirmed using ^{1}H NMR and ^{13}C NMR.

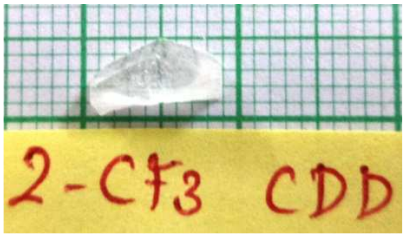

Figure.1 2CF3-CDD crystal grown in tetrahedrafuran

3. Proton NMR

^{1}H NMR (400 MHz, CDCl3): d = 7.672–7.654 (d, J = 6.4 Hz, 2H, CHAr); 7.615–7.577 (t, J = 15.2 Hz, 1H,CHAr); 7.431–7.393 (t, J = 15.2 Hz, 1H, CHAr); 5.279–5.247 (dd, J=8, 4.8, 1H, CH*(OH)); 3.080 (t, J=12H, 1H, CHali); 2.914–2.903 (d, J = 4.4 Hz, 1H, CHali); 2.620–2.558 (m, 2H, CHali); 1.720, (bs, 1H, OH, CH2ali), 1.308–1.129 (m, 15H, CHali).

4. Carbon NMR

^{13}C NMR (100 MHz, $CDCl_3$): d =214.7, 141.1, 132.5,128.0, 127.9, 125.7, 125.7, 70.4, 58.7, 39.2, 27.6, 26.3, 25.8,24.3, 24.0, 23.9, 23.5, 22.4, 21.6.

5. Linear optical property

The grown 2CF3-CDD crystal was subjected to spectral analysis to study the linear optical properties. The recorded absorption spectrum of crystal shows the lower cutoff wavelength at 314 nm and the crystal has found to be wide transparency in the region of 190-1100nm, and it is shown in Fig.[2]. The optical absorption coefficient (α) was calculated the following relation α=2.303log (1/T)/d, where T is the transmittance and d is the thickness of the crystal. The absorption coefficient of the crystal suggests the occurrence of direct band gap, obey the following relation $(\alpha h\gamma)^2=A(h\gamma-E_g)$. The variation of $(\alpha h\gamma)^2$ and photon energy provide the energy band gap (E_g), to extrapolate the linear part from the maximum absorption end, and the energy gap is found to be 3.9276eV. The extinction coefficient is calculated in terms of absorption coefficient, K=λα/4Π. The frequency response of the crystal is obtained in terms of the absorption coefficient and refractive index, σo=αηc/4Π. Reflectance(R) of the crystal has been measured in terms of absorption coefficient by using the relation, $R=1\pm Sqrt\ (1-exp\ (-\alpha t)\ +exp\ (\alpha t))/1+exp\ (-\alpha t)$,Whereα is absorption coefficient and t is the thickness of the crystal. The refractive index (n) was measured in terms of reflectance from the equation.$n=-(R+1)\pm Sqrt(3R^2+10R-3)/2(R-1)$.The refractive index measurements ofthe single crystals were measured using Abbe refractometer. The refractive index measured at ambient temperature (301.2 K) for the single crystals was measured to be 1.609[4,5].

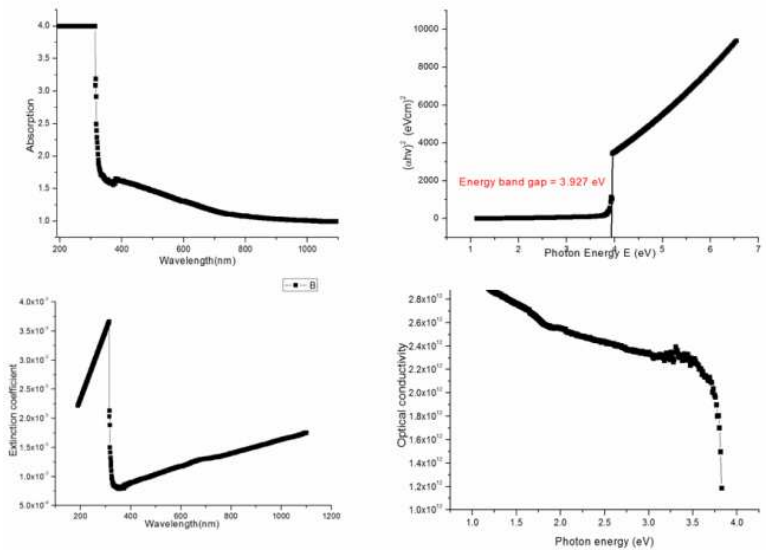

Figure.2. Absorption spectrum and optical constant of 2CF3-CDD crystal

6. Nonlinear optical property

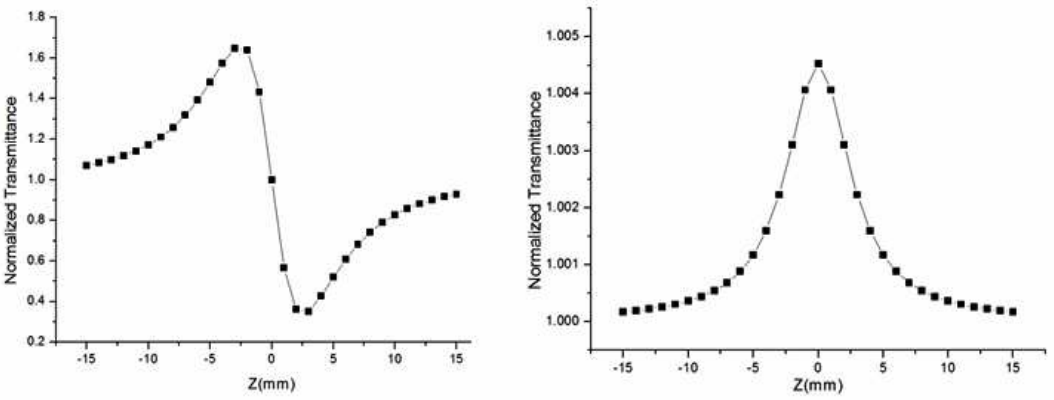

Figure.3. open and closed aperture method of 2CF3-CDD crystal

Z-scan technique is an accurate method to determine both nonlinear absorption and nonlinear refraction of crystals, thin films and liquid solutions developed by shakebahaeet.al.The z-scan technique is intensity dependent refractive index of material and the variation of the refractive index as a function of the incident beam irradiance are given by $n= n_o+n_2I$, where n_o is the linear index, n_2 is nonlinear index of refraction, I-intensity of irradiance laser beam within the sample. When the saturation absorption occurs, the absorption coefficient α is no longer constant; instead it becomes a function of the extinction intensity as in the relation $\alpha=\alpha o+\beta I$. The third order susceptibility (χ^3) is considered as complex quantity, and it is defined as $\chi^3 =[Re (\chi^3)^2+Im (\chi^3)^2]^{1/2}$. The experimental measurements of n_2 and β are allowed to determine the real and imaginary parts of the third order nonlinear optical susceptibility χ^3, according to the following relations $Re (\chi^3) =10^{-4} \varepsilon_o C^2 n_o {}^2 n_2 / \Pi$(cm^2 /W) and $Im(\chi^3)=10^{-2}\varepsilon_o C^2 n_o {}^2\lambda\beta/4\Pi^2$(cm/W)[6].The nonlinear optical effects were due to the thermal mechanism processes of the incident laser power passing through an optical material. In open aperture method, 2CF3-CDD crystal shows a strong saturation absorption peakas shown in Fig[3]. In closed aperture method, the self-defocusing effect of sample shows the transmittance peak is followed by valley and it is shown in Fig [3]. The calculated value of the nonlinear refractive index (n_2) is 1.684X10 $^{-5}$ m^2/W. The nonlinear absorption (β) of the crystal is found to be 9.82X10^{-4} m/W. The third order nonlinear susceptibility (χ^3) of the crystal is 8.535X10^{-6} esu. Two figures of merit, W and T, have been calculated to be W=41>1andT=0.2<1, respectively. The nonlinear polarization is depending on the applied field strength. In the same manner mechanism can be explained in terms of nonlinear susceptibility or nonlinear refractive index. The characteristic time scale for nonlinear response of material from the typical value based on n_2 (10^{-11}m^2/W) or χ^3 (m^2/v) is developed by Robert Boyd.As per the characteristic time scale, the crystal is possibly response in 10^{-3} seconds for optical switching devices.

7. Conclusion

2CF3-CDD crystal has been grown by slow evaporation method for opto-electronic application. The magnitude of nonlinear refractive index (10^{-5}m^2/W), nonlinear absorption (10^{-4} m /W) and third order nonlinear susceptibility (10^{-6}esu) has been studied using Z-scan technique. The optical transmission study reveals the cutoff wavelength of the crystal is 314 nm. The spectroscopic characterization of carbon and proton NMR are studied.

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