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Synthesis, Growth, Optical transmission and Thermogravimetric studies of Morpholin-4-ium 3 carboxy-2, 3-dihydroxypropanoate NLO single crystal

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Abstract : A new organic nonlinear optical (NLO) crystal, Morpholin-4-ium 3 carboxy-2, 3-dihydroxypropanoate (M4CDP) was synthesized and good optical defect free single crystals of M4CDP were grown by slow evaporation solution growth method at room temperature for the first time. UV-Vis-NIR spectrum indicates that the crystal has a very good transmittance in the entire visible and near IR regions of the spectrum suggesting the suitability of the material for NLO applications. The absorbance of M4CDP was used to calculate the refractive index n, the extinction coefficient K and both the real ε_r and imaginary ε_i components of the dielectric constant. The TG trace reveals that the material has good thermal stability. Thermodynamic activation parameters were computed from the TG curve using Coats and Redfern and Non linear regression methods, which confirms second order kinetics.

Keywords : growth, crystals, XRD, nonlinear, optical, thermal.

1. Introduction

The rapid development of high powered laser increases the demand for an excellent optical limiter to protect human eyes and sensitive sensor from the intense laser beams [1-6]. Many materials have been designed and studied in order to attain an excellent optical limiting performance. These materials include semiconductors, inorganic metal clusters and organic molecules [7-8]. Therefore organic molecular materials have been subject to extensive research in this field and have highly sought after non-linear coefficients [9]. Additionally organic crystals with aromatic rings has high non optical linearity, fast response, tailor made flexibility, low mobility, large band gap and higher damage threshold when compared to inorganic NLO materials. Moreover organic molecular crystal shows a strong predilection towards centrosymmetric organization. Even though no direct relation has been found between the ground state dipole moment of the molecules and the preference of symmetric lattice formation, electrostatic interaction would generally promote anti-parallel organization of dipolar molecules [10]. While octopolar molecules provide one strategy towards non centrosymmetric crystals [11], many approaches has been reported to achieve non centrosymmetric crystal lattice formation. These include utilization of chirality and incorporation of bulk substituents [12-16]. In view of this fact and the general preference of origin, molecules towards noncentrosymmetric organization noted above, noncentrosymmetric assembly of a chiral molecule is a matter of considerable interest, especially in the context of developing new materials for NLO applications. Systematic analysis of the intermolecular interactions which drive such organization is an important exercise among the organic crystals. M4CDP is an intriguing one, since among its simple salts one finds the existence of noncentrosymmetric structures. In the present investigation we have synthesized, grown and characterized M4CDP single crystals for the first time by slow evaporation technique. In the present investigation, we report the growth of M4CDP, UV-Vis-NIR and thermal analysis studies.

2. Synthesis and growth

Cold absolute methanol was added to 2,3 di hydroxyl 1,4- butdioic acid. The acid was dissolved by heating the mixture on a hot plate with stirring maintained at a temperature of 85°*C*. The solution was cooled to 25°*C* and morpholine was added drop wise. The product M4CDP was precipitated out of the solution immediately as a white tiny seed crystals by spontaneous nucleation. The nucleated transparent seed crystal was immersed in the solution taken in a beaker using nylon thread and then allowed to grow into a bigger size. The beaker was closed

using a perforated cover having tiny holes, to facilitate the slow evaporation process at room temperature by seeding supersaturated solution and evaporating the solvent. Optical defect free single crystal of dimensions 8x6x3x mm^3 was harvested in a period of a week. The photograph of as grown crystals of M4CDP was shown in Figure*1*.

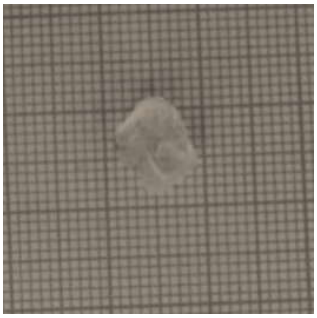

Figure 1. Photograph of as grown crystal M4CDP

3. UV-Vis-NIR studies

The UV-Vis-NIR spectrum M4CDP crystal was recoded using an UV-Vis-Spectrophotometer (model: Varian Cary 5E). The spectrum is shown in Figure*2a*. From the spectrum it is seen that the crystal has a very low cut-off wavelength of 240*nm*. The spectrum further indicates that the crystal has a wide optical transmission window from 330 to 880*nm*.

The measured transmittance (*T*) was set to calculate the absorption coefficient (α) using the formulae

$$\alpha = \frac{2.3026\, log(1/T)}{t} \qquad \text{.....(1)}$$

where *t* is the thickness of the sample in m. The extinction coefficient (*K*) can be obtained from the following relation

$$K = \frac{\lambda \alpha}{4\pi} \qquad \text{.....(2)}$$

The extinction coefficient increases with energy. It has an inverse dependence with*E* in the low energy range (Figure *2b*). The transmittance *T* is given by [17]

$$T = \frac{(1-R)^2 e^{(-\alpha t)}}{1 - R^2 e^{(-2\alpha t)}} \qquad \text{.....(3)}$$

The reflectance (R) in terms of the absorption coefficient can be obtained from the above equation. Hence

$$R = \frac{e^{(-\alpha t)} \pm \sqrt{e^{(-\alpha t)}T - e^{(-3\alpha t)}T + e^{(-2\alpha t)}T^2}}{e^{(-\alpha t)} + e^{(-2\alpha t)}T} \quad \text{.....(4)}$$

The refractive index (n) can be determined from the equation below

$$n = \frac{-(R+1) \pm 2\sqrt{R}}{(R-1)} \quad \text{.....(5)}$$

The refractive index (n) is 1.22 at 240 *nm* for M4CDP crystal.

From the optical constants the electric susceptibilityχc can be calculated according to the relation [18]

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_c = n^2 - K^2$$
$$\chi_c = \frac{n^2 - K^2 - \varepsilon_0}{4\pi} \quad \text{.....(6)}$$

where ε_0 is the dielectric constant in the absence of any contribution from free carriers. The value of electric susceptibility χ_c is 0.079 at λ= 240 *nm*. The real part of dielectric constant ε_r and imaginary part of dielectric constant ε_i can be calculated using relations [19].

$$\boldsymbol{\varepsilon_r = n^2 - K^2 \ and \ \varepsilon_i = 2nK} \quad \text{.....(7)}$$

The value of real ε_r and imaginary ε_i dielectric constant at λ= 240 *nm* are 0.999 and 3.46 x 10^{-3} respectively.

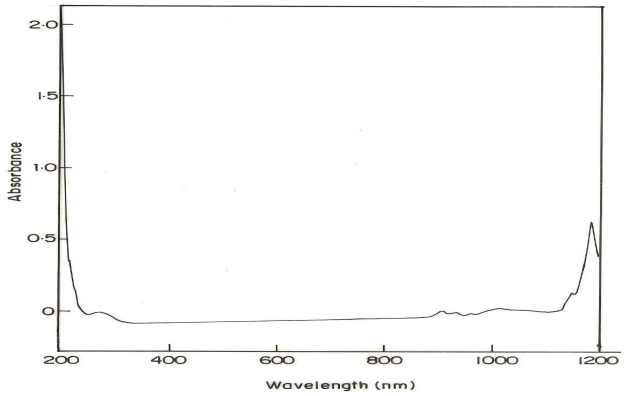

Figure *2a*. UV-Vis-NIR absorption spectrum

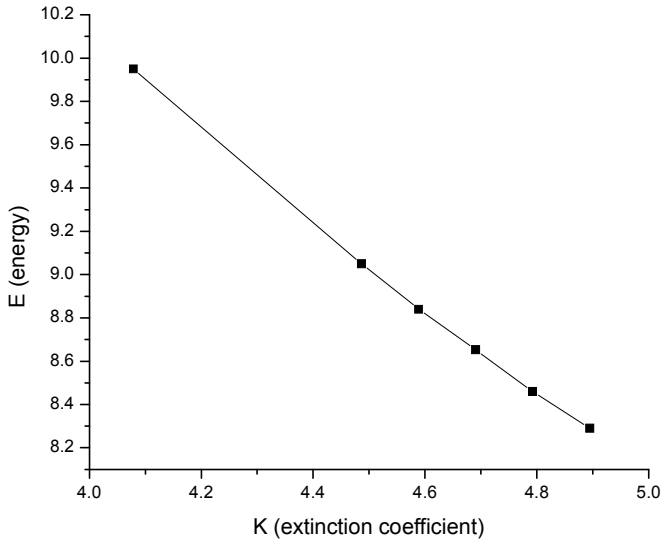

Figure 2b. Variation of energy E with extinction coefficient K

4. Thermogravimetric analyses :

Thermogravimetric analysis (TGA) was carried out using NETZSCH STA 409C analyzer at a heating rate of 25 *K/min* in nitrogen atmosphere for the temperature range 0 to 1400*°C*. The TGA curve shows (Figure 3*a*) that the material has very good thermal stability up to 106*°C*. A sharp exothermic peak in DTA around 108°*C* with at any weight loss corresponds to the melting point of the material. The find decomposition starts 220°*C* and ended up around 450°*C* at which the material loses its complete weight due to the dissociation of carbon network [20]. In the kinetic study of the sample, kinetic parameters such as activation Energy (E_a), reaction order (*n*) and frequency factor (*A*), were calculated using the integral method proposed by Coats-Redfern by Santos et al [21], and the Non-Linear Regression method from Santos et al [22], based on the mass variation of the samples as a function of temperature. The calculation of kinetic data by thermogravimetry.

$$\frac{d\alpha}{dt} = k\alpha^n \qquad \text{.....(8)}$$

where α is the amount of sample undergoing reaction, *n* is the reaction order and *k* is the specific rate constant. The temperature dependence of *k* is expressed by the *Arrhenius Equation*

$$k = Ae^{-\left(E_a/RT\right)} \qquad \text{.....(9)}$$

where A is the Arrhenius constant, E_a is the activation energy and R is the gas constant. From the *Equations (8)* and *(9)*

$$\frac{d\alpha}{dt} = Ae^{-\left(E_a/RT\right)}f(\alpha) \quad \text{.....(10)}$$

where $f(\alpha) = \alpha^n$.

The linear *Equation* is

$$\frac{dT}{dt} = \phi \quad \text{.....(11)}$$

Combining *Equation (10)* with *Equation (11)*

$$\frac{d\alpha}{dT} = \left[\frac{A}{\phi}\right]e^{-\left(E_a/RT\right)}f(\alpha) \quad \text{.....(12)}$$

Integrating *Equation (12)*, the theoretical basis for kinetic calculations by non-isothermal methods (integral and approximation) is obtained.

$$g(\alpha) = \frac{A}{\phi}\int_0^T e^{-\left(E_a/RT\right)}dT \quad \text{.....(13)}$$

where A is the frequency factor, T is the temperature, R is the gas constant, Φ is the heating rate and E_a is the activation energy. The reaction order where n= 2, relate to the most appropriated mechanism is presumed to lead to the best linear plot, from which the activation energy is determined. The equations used for analysis of thermal decomposition reactions are presented below.

$$log = \left[\frac{-\ln(1-\alpha)}{T^2}\right] = log\frac{A}{R} - \frac{E_a}{2.303(RT)} \quad for\ n = 1 \quad \text{.....(14)}$$

$$log = \left[\frac{1-\ln(1-\alpha)^{1-n}}{T^2}\right] = log\frac{AR}{\phi} - \frac{E_a}{2.303(RT)} \quad for\ n\#1 \quad \text{.....(15)}$$

In Non-linear regression method presented by Santos et al, [22], TG/DTA curves for M4CDP crystal was used, besides the following values: $g(\alpha)$, that is just function of α; T, the absolute temperature; T_0, the initial temperature and Φ, the heating rate. Substituting these values in *Equation (13)*, *k (T)* may be estimated, as a function of T, a value of k is found for each value of substituted T

$$g(\alpha) = k(T)\frac{\acute{T} - T_0}{\phi} \quad \text{.....(16)}$$

With the values of calculated *k* and its respective temperature values, a graph of *ln k* versus *1/T* is plotted and the kinetic parameters E_a (activation energy) and *A* (frequency), are calculated according to the *Equation (16)*

$$\ln k = \ln A - \frac{E_a}{RT} \quad \text{.....(17)}$$

The plot of $Y = -log\frac{1-(1-\alpha)^{(1-n)}}{T^2(1-n)}$ versus $x = \frac{1}{T}$ were straight lines for different values of n, however, the best linear fit plot gives the correct values of n. The value of activation energy is obtained from the slope of the best linear fit plot. Figure 3b shows the Coats and Redfern plot. The values of activation energy E, frequency factor A and the order of reaction n are 1315.78 KJ mol^{-1}, 2.15 x 10^{-3} and 2 respectively.

The value of change is standard entropy is obtained by $\Delta S = 2.303\, R \log\left[\frac{Ah}{kT_m}\right]$ where A is the frequency factor, k is Boltzmann constant, h is Planck's constant, R is gas constant, T_m is the absolute temperature in K and ΔS is the standard entropy. The entropy of M4CDP crystal was found to be -299.78 KJ mol^{-1}.

The activation energy (*E*), frequency factor *A*, order of reaction, and the standard change in entropy was found to -833.333 *KJ* mol^{-1}, 2.12 x 10^{-3}, 2 and -299.90 *KJ* mol^{-1} respectively using non linear regression method. Figure 3*c* shows the nonlinear regression method plot of M4CDP. The results suggest that there is a possible change in mechanism of the grown crystal and also the study reveals that the enthalpy is an exothermic process confirming spontaneous type natural reaction.

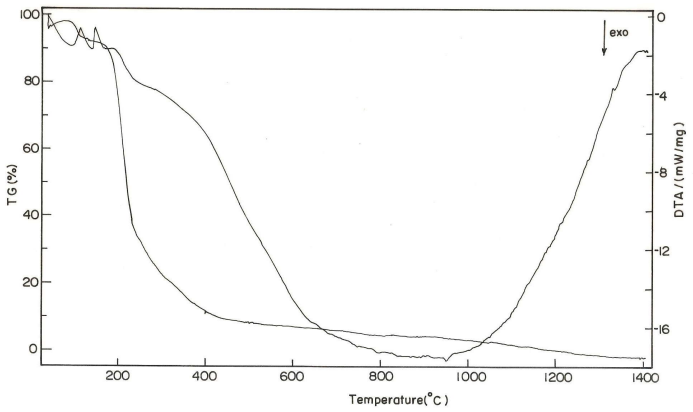

Figure 3a. TG/DTA curves of M4CDP Single Crystal

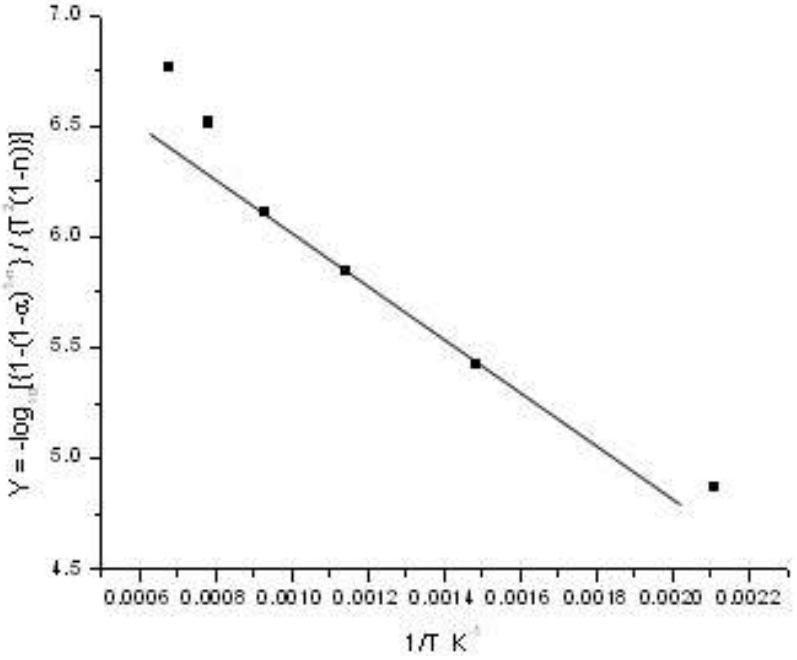

Figure 3b. Coats and Redfern plot for n= 2

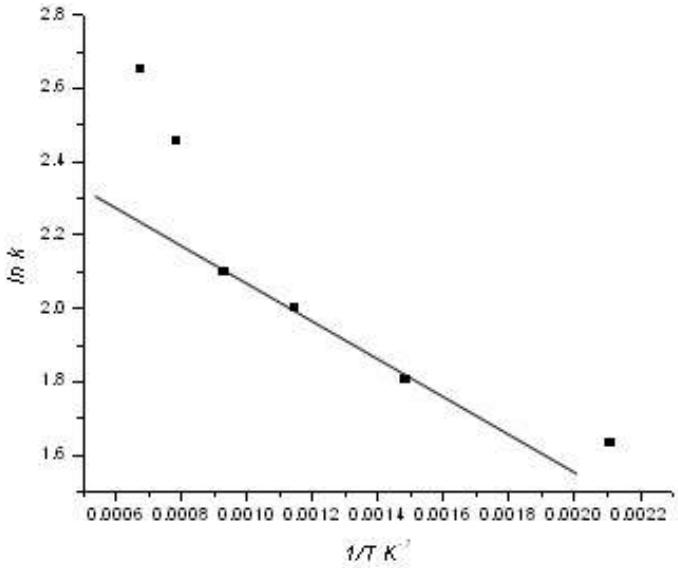

Figure 3c. Non-linear regression plot

Conclusions

The organic material M4CDP was synthesized and good optical quality single crystals were grown by slow evaporation solution growth method at room temperature. Single crystal XRD study establishes the non centrosymmetric which is the root cause for the NLO activity in this organic material. From the optical transmission studies the cut-off wavelength, the extension co-efficient, the refractive index ad the dielectric parameters were determined. The SHG in the grown crystal was confirmed by the emission of green radiation using Nd:YAG laser as the source. The thermal behavior of the crystal was confirmed by TG/DT analyses and kinetic parameters were calculated by applying Coats and Redfern relation and Non-linear Regression methods.

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References

[1] P.Ge. Tang, H.W. Houe, D.L. Long, X.Q. Xin, S.F. Lu, J. Phys. Chem B 101, 27 (1997).

[2] S. Genta, T. Shibahare, H.W. Hong, X.Q. Xin, S. Shu, Inorg. Chem. 34, 4785 (1995).

[3] S. Shu, H.W. Hong, X.Q. Xin, J. Phy. Chem. 99, 4050 (1995).

[4] W.Ji, S. Shi, H.J. Du, P.Ge, S. Tang, X.Q. Xin, J. Phys. Chem. 99, 7297 (1915).

[5] S. Shu, C. Zhangrong, H. Hong Wei, X. Xinquan, Y. Kaibei, Chem. Mater. 7, 1519 (1995).

[6] S. Shu, J.W. Xie, T.C. Chong, H.C. Zeng, J.P. Lany, X.Q. Xin, Mater. Chem. Phys. 39, 298 (1995).

[7] L.W. Tutt, T.F. Boggess, Prog. Quantum Electron 17, 299 (1993).

[8] J.P. Suo, J.E. Riggs, Int. Rev. Phys. Chem. 18, 43 (1999).

[9] A.F. Garito, K.D. Singer, K. Huges, G.F. Lipscomb, S.J. Lalmad, K.N. Derai, Opt. Soc. Am 70,1399 (1980).

[10] J.K. Whitesell, R.E. Danis, L.L. Saunders, J.R. Wilson, J.P. Feagins, J. Am. Chem. Soc. 113, 3267 (1991).

[11] J. Zyss, I. Ledoox, Chem. Rev. 94, 77 (1994).

[12] K. Rieckhoff, W.F. Peticoals, Science 147, 610 (1965).

[13] D.F. Eaton, Science 253, 281 (1991).

[14] B.F. Levine, C.G. Bethea, C.D. Thormond, R.T. Lynch, J.L. Bernstein, J. Appl. Phys. 50, 2523 (1979).

[15] G.F. Lipscomb, A.F. Garito, R.S. Narang, J. Chem. Phys. 75, 1509 (1981).

[16] J. Zyss, J. Phys D 26, B198 (1993).

[17] M.A. Kaid, A. Ashour, Applied Surf. Sci. 253, 3029 (2007).

[18] V. Gupta, A. Mansingh, J. Appl. Phys. 80, 1063 (1996).

[19] M.A. Gaffar, A. Abu El-Fadl, S. Bin Anooz, Physics B 237, 43 (2003).

[20] T. Pal, T. Ker, X.Q. Wang, G.Y. Zhiou D. Wang, X.F. Cheng, Z.H. Yang, J. Crystal Growth 235, 523 (2002).

[21] J.C.O. Santos, A.G. Souza, A.V. Santos, S. Prasad, I.M.G. Santos, J. Food Sci., 67, 1393 (2002).

[22] J.C.O. Santos, A.G. Souza, A.V. Santos, M.F.S. Trindade, 2001, In 5º Mediterranean Conference on Calorimetry and Thermal Analysis, Santiago de Compostela, Eapanha: GECAT, set.