Light absorption in meta-dinitrobenzene and benzyl crystalline films

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This paper presents the optical absorption properties in crystalline meta-dinitrobenzene (m-DNB) and benzil. The optical band gap as an intrinsic property of these crystalline compounds has been studied using UV-VIS Spectroscopy on thin film. Analysing absorption near the fundamental absorption edge we have deduced the wide band gap semiconductor behaviour of these aromatic derivatives. Processing the experimental transmission data using a function obtained by the superposition of a linear function and a power function we have evaluated the band gap energy in m-DNB, $E_g=2.90$ eV and emphasised the same two edges patterns of the light absorption spectrum in benzil deposited on glass as for benzil deposited on quartz, with energetic thresholds slowly moved through lower energies, $E_{g1}=2.79$ eV and $E_{g2}=3.49$ eV. We have also remarked no significant change in the absorption spectrum in benzil induced by the dopant (organic and inorganic).

1. Introduction

Crystalline organic compounds are a class of materials presenting optical, electro-optical and photorefractive phenomena [1-3] offering a large field of experimental application [4-10] and theoretical studies because many particularities of the solid state of these materials are not yet well known and understood. For a large scale of application are preferred crystalline films, because of the complexity and long duration implied by the growth process of organic compounds bulk crystals. Organic films represent an optimum between manufacturing costs and properties for a targeted application. It is not easy to obtain thin films of organic compounds because of some specific properties rising experimental difficulties as low thermal conductivity, anisotropy of the growth speed, supercooling phenomenon and low melting point.

We present in this paper some investigations on the optical absorption properties of 2 types of aromatic derivatives crystalline films using UV-VIS transmission measurements. We have studied organic compounds containing 1 and 2 aromatic rings with substituent groups disturbing the electronic cloud symmetry, respectively meta-dinitrobenzene (m-DNB) and benzil.

2. Experimental

Taking into account all the properties of the organic compounds emphasised above we have selected [11] and experimented a special method to grow films from organic compounds with a melting point $T_{melting}<100\ ^oC$, between two quartz or glass plates by a rapid thermal solidification process (temperature gradient for solidification: $\Delta T>50\ ^oC$, to counteract the supercooling). The crystalline fragments were melted directly between two glass or quartz plates using the hot plate technique and then were rapidly frozen using the cold plate technique, resulting films with dendritic structures.

As starting materials have been used crystalline fragments of pure and doped molecular crystals of m-DNB ($T_{melting}=89.9\ ^oC$) and benzil ($T_{melting}=95\ ^oC$) grown by vertical recrystallization using Bridgman-Stockbarger method. The high purity of these organic compounds has been achieved utilizing chemical purification, vacuum distillation and zone refining (15 passes for m-DNB and 10 passes for benzil). Details about these methods have been presented in previous papers [12,13]. Films of pure meta-dinitrobenzene, pure and doped benzil have been grown between two plates (of glass or quartz). The thickness of the films varied in a large range, $15\div94\ \mu m$, and has been evaluated from geometrical considerations (the area of the films) knowing the density of m-DNB and benzil in the solid phase and assuming that the total volume of substance didn't change during the melting-solidification cycle.

Optical properties of organic crystalline films have been investigated at room temperature with a double beam, computer assisted, Perkin-Elmer Lambda 25 Spectrophotometer.

3. Results and discussion

These organic films have a specific columnar structure with large dendrites branches in their plane, because of the anisotropy and the low thermal conductivity of the investigated organic materials. The direction of the thermal flow is perpendicularly to the quartz plates and films surfaces. A partial order was induced in these films by the same crystallographic orientation of the directions of dendrites growth.

We have studied the properties of the light absorption in m-DNB and benzil in connection with the particularities

of the chemical structure and the strength of the bonding. To investigate the effect of the substrates on the properties of the film, the results obtained by optical characterisation of m-DNB and benzil films grown between glass plates have been compared with those of the films obtained between quartz plates. We have emphasised in benzil a special shape with two edges of the fundamental absorption, (Fig. 1a). The pattern of the differential absorbance (Fig. 1b) has confirmed the existence of a subband light absorption structure with the peak situated at 380 nm, correlated with the particularities of the molecular structure, being assigned to dicarbonyl groups absorption in benzil. The strong interaction between the carbonyl groups in the solid state has produced a splitting in two components of the energetic level (n-π*) in dicarbonyls, that corresponds to the two edges of the absorption process in benzil [14]. The transmission spectrum in m-DNB thin film is characterized by a steep, practically no structured absorption edge (Fig. 2) in agreement with the result presented in a previous paper [15]. Benzil, as the major part of organic molecular materials [16,17], is characterised by weak van der Waals bonding forces and weak superposition between the orbitals π of the molecules generating a narrow peaks absorption spectrum in the UV range (Fig. 3) and a structure with wider energetic bands than m-DNB.
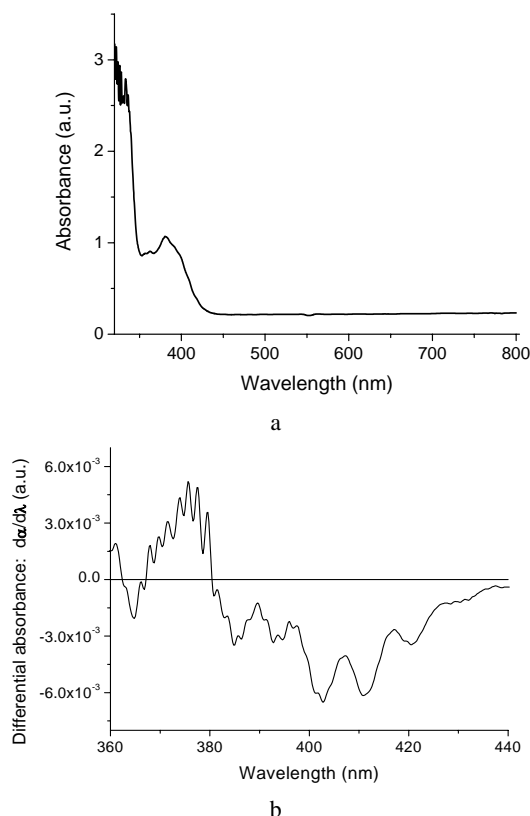

a

b

Fig. 1. a) Absorption spectrum of pure benzil film (33 μm) grown between two z-cut quartz plates. b) Differential absorbance spectrum in benzil film.

On the contrary, the m-DNB spectrum, more similar to that of a classical semiconductor, can be justified by stronger interactions between the polar molecules and partial superposition of the π orbitals in neighbour molecules that generates a structure with narrower valence and conduction bands.
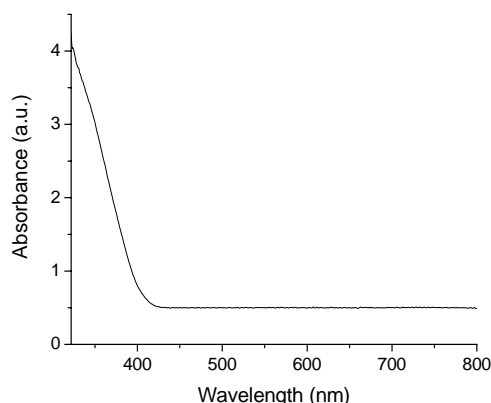

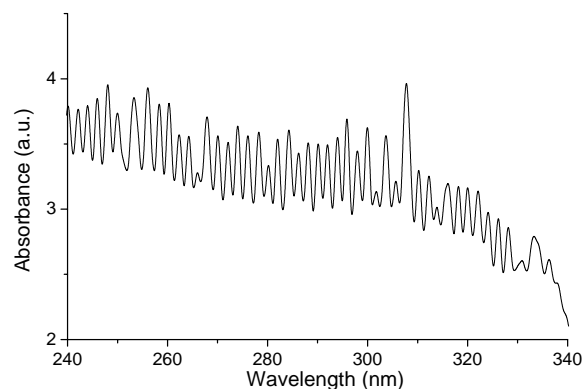*Fig. 2. Absorption spectrum of pure m-DNB film (15 μm thickness).*

Fig. 3. UV absorption spectrum in benzil film (33μm thickness).

We also have investigated the effect of the impurities on the light absorption spectrum in benzil films (Fig. 4) grown between quartz plates. The most important property of the light absorption in benzil is the existence of the two absorption edges (Fig. 4a). The fundamental absorption at the edge with the higher energetic threshold is strongly attenuated in benzil doped with m-DNB and sodium, compared to pure benzil, because of the light diffusion on the nonhomogeneities of the films with different thickness: 61 μm respectively 94 μm. No important change near the second absorption edge with lower energetic threshold has been emphasised in the pattern of the absorption edge through the introduction of specific energetic bands in the band gap by doping with influence on the intrinsic property of the organic compound (Fig. 4 b,c). The doping with Na only has reduced significantly the intensity of the absorption compared to the doping with m-DNB (Fig. 4 b,c) because of the impurity segregation [18]. Sodium is not completely dissolved and generates microinclusions as distinct phase in benzil. Comparing these results with those presented in [14] obtained on films grown between glass plates we can conclude that the two edges shape of the fundamental absorption in benzil has remained unchanged, independent of the nature of the plates [14].
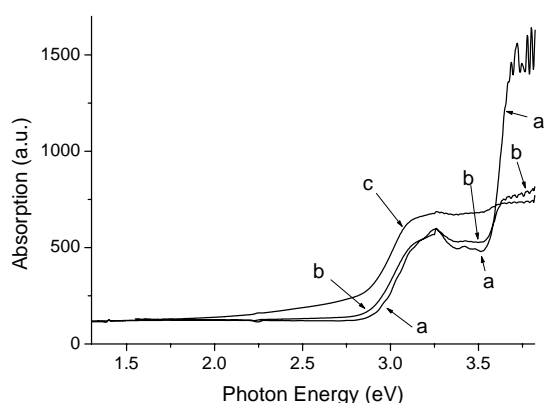
Fig. 4. Comparative absorption spectra of: (a) pure benzil film (33 μm) grown between two z-cut quartz plates, (b) benzil doped with m-DNB (c=3 wt%) film (61 μm) grown between two yz quartz plates and, (c) benzil doped with Na (c=6 wt%) film (94 μm) grown between two yz quartz plates.

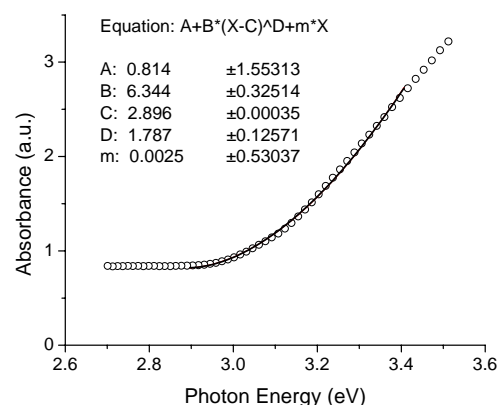*Fig. 5. Experimental data fitting for sample of pure m-DNB film (15 μm) grown between two glass plates using function (1).*

Absorption data near the fundamental absorption edge give us information on the band gap energy and help us in identifying the semiconductor behaviour of these organic solids [19]. The wide optical band gap, E_g=2.90 eV in meta-dinitrobenzene, results from the experimental data fitting (Fig. 5), using the bellow formula obtained by the superposition of a linear function and a power function:

$$\alpha(E) = a + b \cdot (E - c)^d + m \cdot E \qquad (1)$$

where E is the photon energy, α is the absorption coefficient, c is the band gap energy E_g, d is a coefficient depending on the absorption mechanism and the baseline (a+m·E) is associated with all the other parasitical processes affecting the band to band absorption, as scattering of the light on the nonhomogeneities of the sample, having a slow variation with the energy.

The shape of the transmission spectra (Fig. 5) is practically unchanged in thin film compared with bulk samples of m-DNB [20], but the edge of the fundamental absorption is slowly shifted through red in bulk m-DNB sample because the weak absorption in the low wavelength region in thin film become important for bulk sample [21].
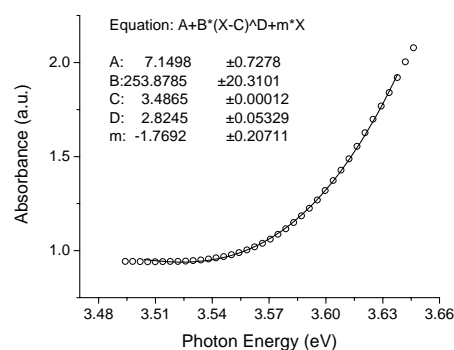
The shape of the absorption edge is also independent on the plates (glass or quartz) used to prepare m-DNB films, only small variations in the band gap energy (ΔE_g=0.024 eV) and no significant changes in the absorption mechanism closed to absorption by indirect transition (coefficient variation from d=1.83 to d=1.78) being evidenced.
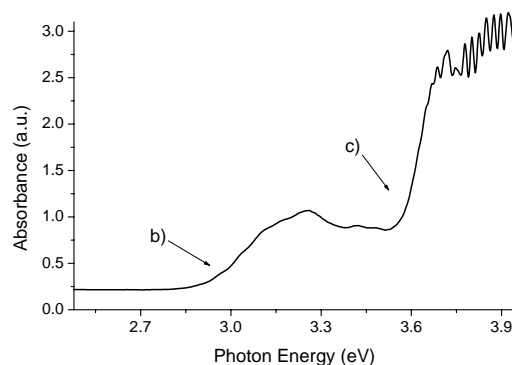
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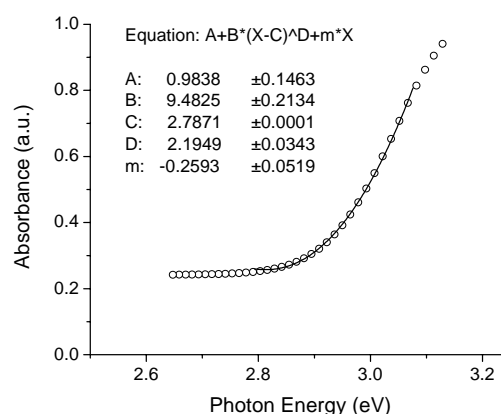
b

c

Fig. 6. a) Absorption spectrum of benzil film between: 2.6÷3.3 eV. b), c) Experimental data fitting for film of pure benzil using function (1) for two different energy ranges: b) 2.6÷3.1 eV; c) 3.49÷3.65 eV.

The absorption spectrum of benzil film has shown the presence of two absorption peaks at the absorption edge (Fig. 6a). The same analytical procedure for benzil film has evidenced the existence of two energetic thresholds E_{g1}=2.79 eV (Fig. 6b: fitting parameter c) respectively

E_{g2}=3.49 eV (Figure 6c -fitting parameter c) for the two absorption edges for film grown between glass plates.

However, using different plates (made of glass, or quartz) to prepare the benzil films we have remarked some variations in the values of the two thresholds energies (ΔE_{g1}=0.05 V and ΔE_{g2}=0.063 eV) and in the coefficients associated with the absorption mechanism which vary from d=1.86 to d=2.19 suggesting an absorption process more closed to an indirect transition for the first absorption threshold and from d=1.57 to d=2.82 suggesting a modification from direct to indirect absorption process for the second absorption threshold.

Table 1. Comparative presentation of the fitting parameters of the experimental absorption data for pure m-DNB and pure benzil film for two energy ranges, on different substrates using function (1).

Organic compound	Type of plates			
	Glass		Quartz	
	c (eV)	d	c (eV)	d
m-DNB	2.89684	1.78704	2.92133 [14]	1.83623 [14]
Pure benzil (energy range 2.6÷3.1 eV)	2.78716	2.1949	2.83799 [14]	1.86257 [14]
Pure benzil (energy range 3.49÷3.65 eV)	3.48657	2.82455	3.54978 [14]	1.57764 [14]

The signification of the parameters is given in the text, Eq. (1).

4. Conclusions

A melt recrystallization method was developed for getting thin film of low melting point organic compounds (meta-dinitrobenzene and benzil) between two glass or quartz plates. Processing the experimental data with a function obtained by the superposition of a linear function and a power function we have evaluated the optical band gap energy, E_g=2.90 eV, and emphasised the classical semiconductor behaviour of m-DNB film grown between glass substrates. We have evidenced in benzil thin film on glass a light absorption process with the same two edges as for benzil grown on quartz substrates, corresponding to different energetic thresholds slowly moved through lower energy, E_{g1}=2.79 eV and E_{g2}=3.49 eV, determined by molecular structure and the strength of the binding force between different dicarbonyl groups and which is independent of the nature of the substrates (glass or quartz). A significant change in the intensity of the absorption in benzil has been remarked by doping because of the light diffusion on defects, and of the nonhomogeneities of the films, as a result of impurity segregation.

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