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Section 2: Organic materials

SOME OPTICAL INVESTIGATIONS ON CRYSTALLINE DOPED META-DINITROBENZENE

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This paper presents some investigations on the organic crystal growth process from the melt. There is a strong connection between the growth process, the crystalline quality and the physical properties of bulk crystalline meta-dinitrobenzene. Different physical defects can be induced by different growth conditions and different purity of the material. Compositional nonhomogeneities are determinative from optical properties of the crystalline material. The scattering process in crystalline meta-dinitrobenzene doped with oxine has been analyzed from the point of view of Kubelka-Munk theory using reflectance spectroscopy. This can offer us data on the micro nonhomogeneities' generation during the growth process of organic crystal.

Keywords: Organic nonlinear crystal growth, Bridgman-Stockbarger, Meta-dinitrobenzene, Dopants, Optical properties, Kubelka-Munk theory

1. Introduction

Disubstituted derivatives of benzene are used as optical nonlinear material replacing the inorganic classical compounds. The most important characteristics of these organic crystalline materials are: high values for the nonlinear coefficients, large birefringence values, very high damage thresholds in power laser beam and large transparency domain between UV-VIS. The most of the molecules for nonlinear optics derives from an aromatic nucleus showing a system of delocalized π electrons. The solid-state properties of the compounds are influenced by the nature of the substituent and the modus of molecular packing. The optical nonlinear materials requirements ask for a large difference in dipole moment characterizing the interaction between substituent group and electronic cloud, between the ground and excited states of the molecule organized in a non-centrosymmetric structure.

The principal constrains to good crystal growth are that crystal should be pure and homogeneous from the point of view of their properties. Some competing factors defining the growth process are determinative for nonlinear optical properties of organic materials. It is very important to study the effect of these parameters on the crystal quality. A lower quality material grown easily but in very well established conditions can be used to estimate the potential of a particularly grown material and the non-linear behaviour. It is important to discuss the role of the thermal regime in the definition of a crystal of high optical and structural perfection. The optical crystal must have good transparency and large size.

Meta-dinitrobenzene (m-DNB) is a disubstituted aromatic compound with the following characteristic: a melting point of 89.8 ^{o}C, a transparency range between 0.4-2.5 μm. In a crystalline form is a negative biaxial crystal and belongs to the point group symmetry mm2 and space group $Pbn2_1$. As dopant we have used an organic compound with a molecule similar to m-DNB molecule.

2. Experimental

To grow crystals of m-DNB we have used an organic material synthetized in our laboratory. To obtained the necessary purity degree this material has been purified using chemical and physical methods. More details concerning these processes are presented in the paper of A. Stanculescu and cool [1]. The growth from the melt method is indicated because the growth rate is high and the crystals are more pure and adequate for optical applications. The crystallization processes are: an horizontal directional solidification and a vertical Bridgman-Stockbarger growth.

To control the growth process we have to control the following parameters:

- the thermal regime characterized by a high thermal gradient across the growing zone;
- the geometry and the material (Teflon, quartz), of the growing chamber affected by the anisotropy of the growing speed and the adhesion to the wall;
- the moving regime asking for a small lowering speed of the ampoule in the thermal gradient to remove the solidification heat from the solid-liquid interface.

The first experiment was a directional solidification in horizontal configuration in the below conditions:

- molten zone temperature: 90-110 ^{o}C;
- molten zone length: 2.5 cm;
- molten zone moving speed; 3 cm/h.

Crystal growth equipment characteristics and modification for a Bridgman-Stockbarger growth are detailed in the paper of A. Stanculescu and coll. [1]. To grow organic crystal we must satisfy the following conditions after D. Fox and coll. [2]:

-a steep thermal gradient to counteract the supercooling phenomenon characteristic for organic compounds;

-a slow moving speed to assure the dissipation of the melting heat by a low thermal conductivity material avoiding the twins, additional nucleation and inclusions generation.;

-a teflon crucible to avoid the adhesion to the ampoule walls;

-a special configuration of the ampoule to induce and select the nucleation.

We have studied the Bridgman-Stockbarger crystallization of our organic compound, m-DNB, in different experimental conditions:

- furnace maximum temperature (the hot zone): 1) 114 ^{o}C; 2) 110 ^{o}C; 3) 110 ^{o}C; 4) 110 ^{o}C; 5) 115 ^{o}C;
- thermostat- bath temperature (the cold zone): 1) -; 2) 50 ^{o}C;3) 50 ^{o}C; 4) 50 ^{o}C; 5) 50 ^{o}C;
- the thermal gradient at the melt-solid interface: 1) 3 ^{o}C; 2) 5 ^{o}C; 3) 4.5 ^{o}C; 4) 6.6 ^{o}C; 5) 8.5 ^{o}C;
- the ampoule moving speed: 1) 7 mm/h; 2) 1.3 mm/h; 3) 1.2 mm/h; 4) 1 mm/h; 5) 1 mm/h.

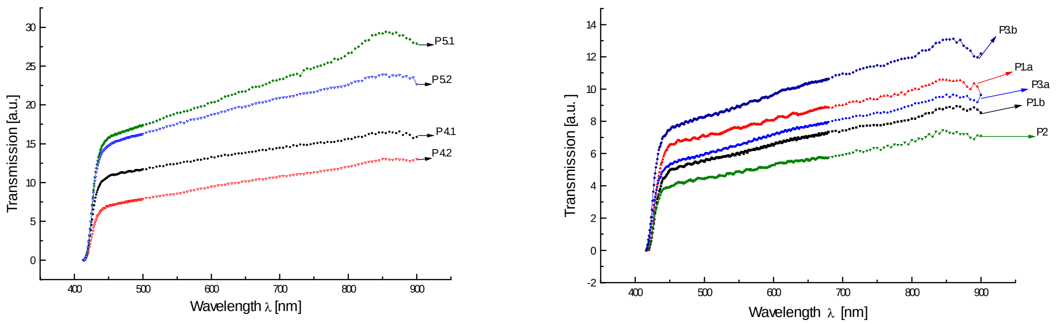
As dopant we have used an organic compound with a molecule similar to meta-dinitrobenzene molecule. Oxine has a melting point of 72-74 ^{o}C and a molecular weight of 145.16 g/mol (m-DNB) has a molecular weight of 110.11 g/mol). We have work in the conditions of a low doping: 0.006 g of oxine in 0.6 g of m-DNB. The growth conditions for oxine doped meta-dinitrobenzene crystals in a Bridgman-Stockbarger configuration have been presented by A. Stanculescu and coll. [3]. As-grown ingots have been sliced in wafers polished with a mixture of ethylenglycol - alumina powder of different size (5 μm and then 0.5 μm).

Optical characterization of the pure and doped meta-dinitrobenzene was realized by bulk UV-VIS transparency and reflectance measurements, using a SPECORD M 42 apparatus. Samples have a thickness is between 0.5 mm and 1.3 mm. We have used the set-up for Diffuse Reflectance Spectroscopy in a 45/0 configuration in concordance with G. Kortüm [4]. We have calibrated the apparatus on the scale 100% SPEC using $BaSO_4$ as the comparison standard and a “milky glass” sample as a reference sample assuring the reproducibility. The standard surface treated-milky-glass have a reflectivity constant over a long period, using suitable care and cleanliness. The reflectance measurements were made in the conditions of a black background (R_0), and these values have been used to calculate the effective reflectance (R) and the scattering coefficient (S) from Kubelka-Munk (K-M) theory.

3. Results and discussions

Optical measurements have been performed on wafers and are strongly depending on the structural quality of the material and on the quality of the surface processing. Transmitance and reflectance spectroscopy offered us many data on the macro and micro nonhomogeneities' generation in the process of organic crystal growth. The growth parameters defined by the experimental conditions have a big impact on the quality of m-DNB crystalline material. In the crystal growth process from the melt, the growth conditions are modified in connection with the experimental set-up (a Bridgman-Stockbarger installation, a directional solidifying installation), the thermal gradient at the interface between the solid and the melt, the speed of the quartz ampoule moving in the thermal gradient, the geometry and the material of the crucible containing the charge introduced in the ampoule. The most favorable experimental conditions, as have been presented by A. Stanculescu and coll. [3], for an homogeneous Bridgman-Stockbarger ingot grown in nearly stationary conditions, having better optical quality are:

-a steeper gradient at the interface: 8.5 ^{o}C;
-a slow moving speed: 1 mm/h.



a) b)

Fig. 1 a, b. Longitudinal (*P1*, P2, *P3*, P4.1, P4.2, P5.1, P5.2) and radial (P1a, P1b; P3a, P3b) variations of transmission properties on undoped meta-dinitrobenzene bulk polycrystalline samples grown by directional solidification in horizontal configuration.

These samples (Fig. 2) show a better radial homogeneity than the samples cutted from directional solidified ingot that presents a larger radial (Fig. 1b) as longitudinal (Fig. 1a) variation of the transmission properties. The ingot directional solidified in an horizontal configuration has a worse mechanical resistance because of the twins and cracks that give a higher fragility of m-DNB. The longitudinal transmission decreases in the following succession: P5>P4>P3>P2>P1, where P_5 is a wafer from the last freezing end of the ingot. The variations in transmission in different points on the same wafer show some macrononhomogeneities of the material with consequences on the optical properties. The crystalline imperfections (structural defects, compositional nonuniformity) become scattering and absorption centers. To improve the growth of good optical quality organic crystals and control the crystallization process it is necessary to control the growth parameters. As have been presented by Stanculescu et al. [3], the presence of dopant (oxine) reduce the transmission by comparison with pure meta-dinitrobenzene, for bulk material samples, supposing an identical surface processing.

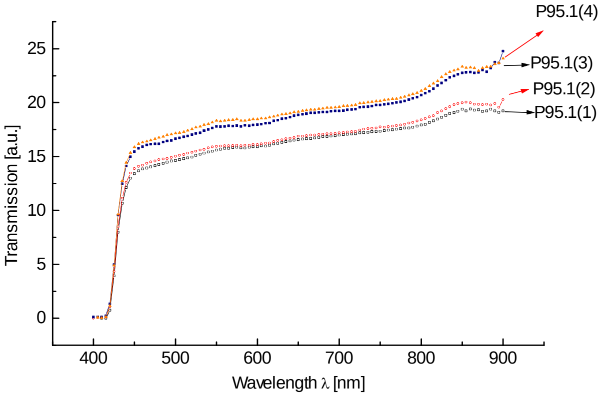


Fig. 2. Longitudinal and radial variation of the transmission properties on pure meta-dinitrobenzene bulk monocrystalline samples grown in a Bridgman-Stockbarger configuration.

long. position↓	radial pos. →	r_A	r_B
I		(1)	(2)
II		(3)	(4)

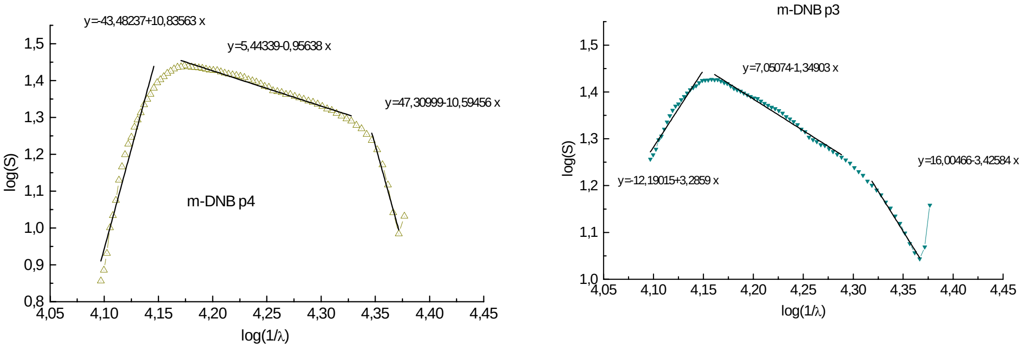
The radial nonhomogeneity of m-DNB crystal doped with oxine is a result of void formation during the contraction of the crystal upon cooling. The doped ingots are less homogeneous than the pure ones because of an unequal distribution of controlled content of impurities between the melt and the crystal during the solidification process. Supposing the same degree for wafers' surfaces processing to avoid any surface diffusion, the ingot presents a strong bulk diffusion because of an uniform distribution in its volume of some compositional micrononhomogeneities. To control the process of microinclusions development in organic material during the crystal growth we have to analyze the following parameters: the purity of the material and the crystallization regime.

A rigorous theory of the scattering exists only for single scattering at particles small compared with the wavelength (Rayleigh) and for isotropical, spherical particles of any size (Mie). To process the diffuse reflectance measurement experimental data we used the K-M theory(a single scattering process) [4]. We have to verify if this theory is, at least qualitatively confirms in our experimental conditions. T he simplifying assumptions, as a basis for application of this theory, are:

-an isotropic distribution of radiation being ignored any regular reflection;

- randomly distributed particles which are much smaller than the thickness of the samples.

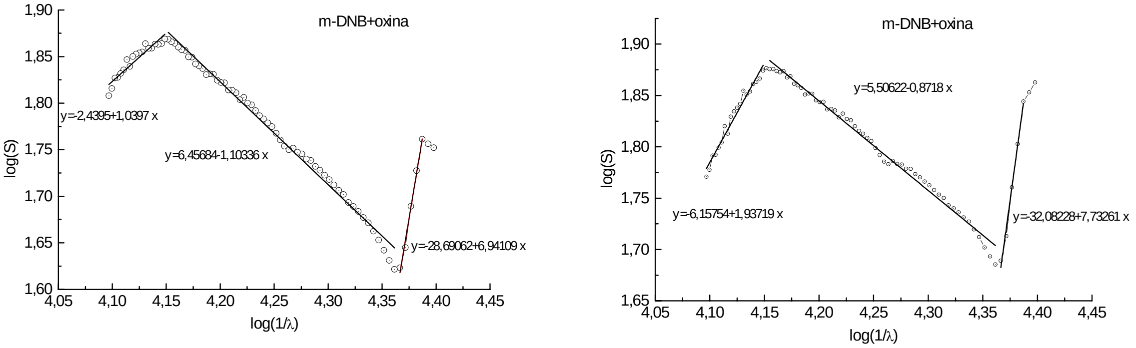
Other supplementary approximations are: a negligible intern reflection interference and a “single scattering” process associated with single particle having a dimension much greater than the wavelength, sufficiently separated from each other (minimum separation twice particle diameter). Diminishing distance between the scattering particles, single scattering gives way to multiple scattering. A criterion to evaluate the type of the scattering mechanism is the apparent absorbance of the sample in transmission measurements. For opaque samples, for which the radiation is practically completely reemitted is predominant a multiple scattering. For large scattering density, Sd, where d is the wafer thickness, for sufficiently great number of particles and larger thickness, ultimately results an isotropic scattering distribution of radiation inside the sample and the approximation of single scattering is valid. In conclusion, for small dens packing particles the scattering process can be described in the manner of a single scattering. The ratio between the absorption coefficient in reflection (K_R) and in transmission (K_T) determined in the approximation of K-M theory takes a theoretical value 2 for an homogeneous medium where K and S are not function of position and the distribution of the scattered radiation is isotropic. For the system adequate to such modeling, this theory can be used to evaluate the dimension of micro nonhomogeneities present in different material. We have plotted log(S) as a function of log(1/λ), where 1/λ is the wave number. In K-M theory the slope of the curve is a qualitative index for the scattering process. For a Rayleigh scattering the slope must to be 4 [4]. The wavelength dependence of the scattering coefficient power is not according to the theory of a single scattering (Fig. 3) for bulk samples of pure m-DNB and of m-DNB doped with oxine (Fig. 4) and we can not evaluate the dimensions of the nonhomogeneities.



a) b)

Fig. 3 a, b. Logarithmic plot of the scattering coefficient S versus wave numbers, for meta-dinitrobenzene sample grown by directional solidification in horizontal configuration.

For m-DNB as grown crystal wafers, this ratio has small values, starting with 0.83 at 23 890 cm^{-1} and ending with values very closed to 0 at 12 500 cm^{-1} and from 0.87 at 23 890 cm^{-1} to values very closed to 0 at 12500 cm^{-1}. For doped m-DNB the ratio takes values between 0.65 at a wave number of 25 000 cm^{-1} and 0.05 at 12 500 cm^{-1}. Repeating the measurements in an another point on the wafer surface we found similar results: a ratio taking values between 0.57 at 25 000 cm^{-1} and 0.03 at 12 500 cm^{-1}. The results confirm the reproducibility of the measuring process. In our case, the ratio K_R/K_T is smaller than 2 also for m-DNB and m-DNB doped with oxine samples that means a material more dens in transmission than in reflection. In fact, in our material, areas with large values of K alternate with areas of small K and the packing density is lower in reflection than in transmission. In consequence, when the material is polycrystalline or presents microinhomogeneities, the real travel path of the wave is changed in an indefinite manner because of the total reflection at the small crystals surfaces. The approximation of single scattering is no more valid and the K-M theory is not applicable.



a) b)

Fig. 4 a, b. Logarithmic plot of the scattering coefficient S versus wave numbers, for oxine doped meta-dinitrobenzene sample grown by Bridgman-Stockbarger vertical configuration.

The conclusions indicate that the approximations of K-M theory are not suitable for the modeling of our crystalline system because in this case we can not use the approximation of a single scattering process to describe our system. Using this theory in analyzing the experimental data, the results are not compatible with the conclusions of K-M theory. This indicates that the experimental system (pure organic crystal grown by directional solidification and doped organic crystal) limits or excludes the application of this theory.

4. Conclusions

We have studied the optical properties in connection with the growth process and the crystalline quality of doped m-DNB. Physical defects are induced using different experimental set-up, thermal regime and growing geometry. The most homogeneous ingot has been grown in a Bridgman-Stockbarger configuration. Transmitance and reflectance spectroscopy offered us many data on the macro and micro nonhomogeneities' generation in the process of organic crystal growth. Reflectance Spectroscopy gives information on the bulk scattering mechanism on the growth compositional microononhomogeneities. The internal quality of our sample it is not adequate to single scattering mechanism characteristic for Kubelka-Munk theory.

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