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HIGH PURITY ORGANIC FUNCTIONAL MATERIAL FOR CRYSTAL GROWTH

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Abstract. This paper presents a comparative study of the purity evolution after different chemical and physical purification stages for meta-dinitrobenzene as functional material for crystal growth, using complementary methods: X-Ray Diffraction, Thermogravimetric analysis, FTIR Spectrophotometry.
Inductively Coupled Plasma Optical Emission Spectroscopy gave us the concentration of metallic impurities.

Key words organic compound, purity, X Ray Diffraction, Thermogravimetry, FTIR, ICP Optical Emission Spectroscopy

A purity study of meta-dinitrobenzene for crystal growth

1. INTRODUCTION

Crystalline organic compounds represent a new class of multifunctional materials with interesting simultaneous optical electronic, optoelectronic and photorefractive properties for a wide range of applications. Molecular materials are considered now as a very important alternative for electronic components and electric active devices manufacturing. Energetic structure, electrical and optical properties are determined by their molecular configuration and the particularities of the crystalline construction. For future applications in electronics and optoelectronics it will be necessary to utilize compounds with big molecules, less volatile and in very small geometrical configuration to compete with the modern tendency of the miniaturization. To attempt this aim are very important the crystal purity and quality. The purity requirements for the organic materials are a difficult and open problem that has to be solved [1]. Ordinarily, we can characterize a material after its capacity to crystallize in good, transparent crystalline structures and its spectra in the optical wavelengths range. But these measurements are not very sensitive to the presence of the impurities' traces that can affect the crystal growth process.

An important class of multifunctional organic molecules for optical and electrical applications is benzene derivatives containing one or more aromatic nucleus. In some compounds different substituent groups disturb electronic clouds symmetry giving rise to specific properties.

2. EXPERIMENTAL METHODS

The purity requirements for organic materials utilized in crystal growth are consistent with those specific to inorganic semiconductors, but processes involved are complicated and of long duration.

The raw material was meta-dinitrobenzene (m-DNB) synthesized using purity reagents (purity 98 wt%). Then the organic compound has been purified using different chemical and physical methods:

-selective chemical reaction (with Na_2SO_3) to remove the ortho and para isomers of m-DNB;

-slow vacuum distillation under a vacuum of 10^{-4} torr in dynamic regime;

-two stages directional freezing (length of the molten zone of 2.5-3 cm, traveling average speed of 2,5 cm/h and a number of passages between 6 and 23 in the first stage and between 8 and 14 in the second stage).

During the chemical purification ortho and para isomers are transformed into corresponding sodium salts soluble in water of the mononitrosulphonic acids and can be easily removed. Directional freezing is an efficient purification method only after the preliminary purification processes presented above, because at high concentration impurities can be trapped at the solid-liquid interface generating bands along the ingot. The major impurity in m-DNB is benzofurazan that became benzofurazan-1 oxide (benzofuroxan) in the presence of moisture that can also favors the transformation of isomer ortho of m-DNB in benzofurazan. For these reasons it is necessary to work under vacuum conditions. In the first step of the directional freezing process the impurities with a segregation coefficient $k<1$ accumulate at the end of the ingot and to increase the efficiency of the second step purification process we have to maintain the same traveling direction for the molten zone. More details concerning experimental sets-up and parameters for preparation and purification of m-DNB have been presented by Stanculescu and col. in previous papers [2; 3].

To analyze the purity and the effectiveness of these purification stages on the purity of the material we have used different methods (and apparatus): X-Ray Diffraction measurements (Dron 3 Diffractometer), Thermogravimetric analysis (MOM 1500 D Derivatograph) and FTIR Spectrophotometry (Shimadzu 8201 PC). For X Ray measurements we have used the Lawe powder method for chemical qualitative identification of some components in the samples. In thermogravimetric analysis the sample is continuously weighted when it is heated at a constant speed, resulting the thermogravimetric plot. This is an alternative method to qualitative evaluation of the material purity. IR Spectrophotometry is a complementary method, characterized by a greater sensibility, we have used for qualitative investigation of the purity of m-DNB. We have obtained the FTIR spectra, because of the greatest sensibility of the method, on solid sample: thin film of different purity grown between two silicon wafers. The methods presented above have been used to evaluate the presence of organic impurities but for organic crystals' growth inorganic (metallic) impurities are also very important and can affect the crystallization process. Inductively Coupled Plasma Optical Emission

Spectroscopy has been utilized to measure the content of metallic impurities in m-DNB. More details about this method have been presented in a previous paper by Stanculescu and col. [2].

3. RESULTS AND DISCUSSIONS

A high concentration of organic impurities in the starting material was indicated by the existence of some dark brown bands along the frozen ingots, comparing with the color of the pure material, white-yellow.

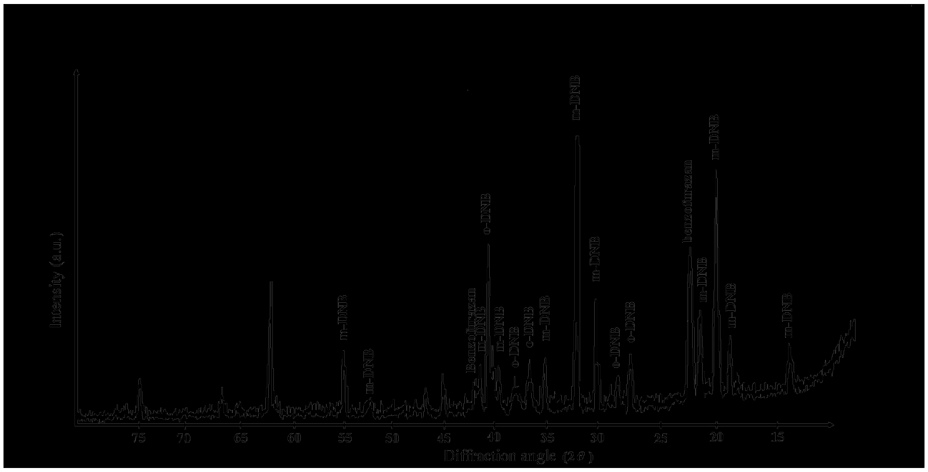
We have effectuated a comparative study on the purity of meta-dinitrobenzene correlating the results obtained using for analyze different methods presented above. X-Ray Diffraction gave us information on the purity of the synthesized, or starting materials and on the evolution of the purity after different purification stages. We have underlined a decrease in the content of the major impurities, ortho-dinitrobenzene and of benzofurazan (a derivate impurity), after successive purification by chemical and physical methods already presented. We have observed (Figure 1: a, b, c) a decrease, by purification, of the peaks associated with the presence of the isomer ortho (40.8^o) and of those associated with the presence of benzofurazan (43^o and 23^o) resulting from ortho-dinitrobenzene reaction with air oxygen and water, and a strengthening of the peaks of meta-dinitrobenzene (41.4^o; 32^o; 21.6^o; 20.2^o and 19^o) as an evidence of the effectiveness of the purification process.

The thermogravimetric analyses coupled with differential thermal analysis indicate an increase of the melting temperature (Figure 2: a, b, c), close to the values from literature ($T_{melting}$=89 ^oC). Higher purity is attained after different purification stages because the impurity lowering the melting temperature with a segregation coefficient k<1 was removed.

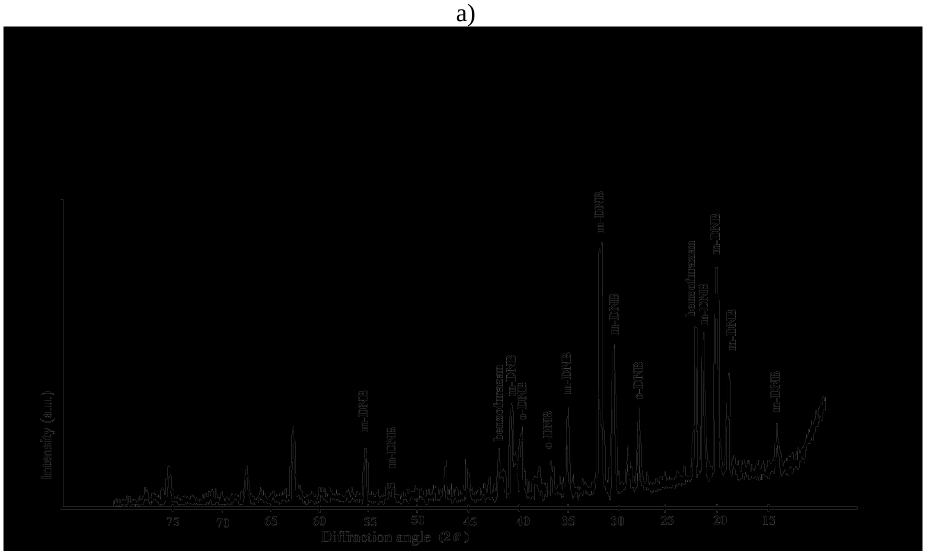
For a higher degree of impurification of the sample (Figure 2 a) we have obtained o lower melting point of the m-DNB sample and a more rapid weight lose process compared with more pure m-DNB sample (Figure 2 b; c).

Information on the evolution of the material's purity along the ingot and on the effectiveness of the purification mechanisms for meta-dinitrobenzene has been obtained also from FTIR Spectrophotometric data (Figure 3). In the top of the ingots concentrate the impurities with k>1 and in the last zone to froze the impurities with k<1.

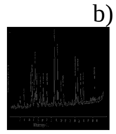
We have remarked significant differences between the spectra realized with sample from the end and the middle of the ingot. For the first sample containing impurity with k<1 we have observed many absorption peaks between 1700 and 2700 cm^{-1}, and wide and structured peaks situated around 1500 and 1350 cm^{-1} (Figure 3 a). For the last sample, of the highest purity, the shape of the spectrum between 1700 and 2700 cm^{-1} is approximately a line, the absorption peaks' number and position being in concordance with those indicated in the literature [4].



a)

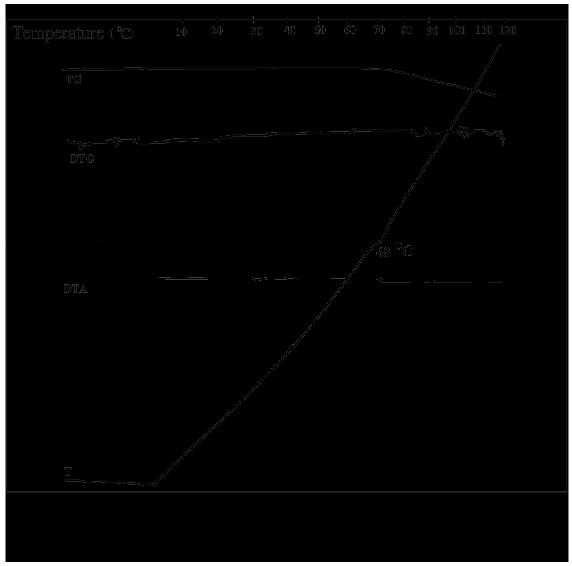


b)



c)

Figure 1 - X-ray diffraction spectra on m-DNB: a) as synthesized; b) chemical purified; c) directional solidification purified


Temperature (°C)
10 20 30 40 50 60 70 80 90 100 110 120
TG
DTG
68 °C
DTA
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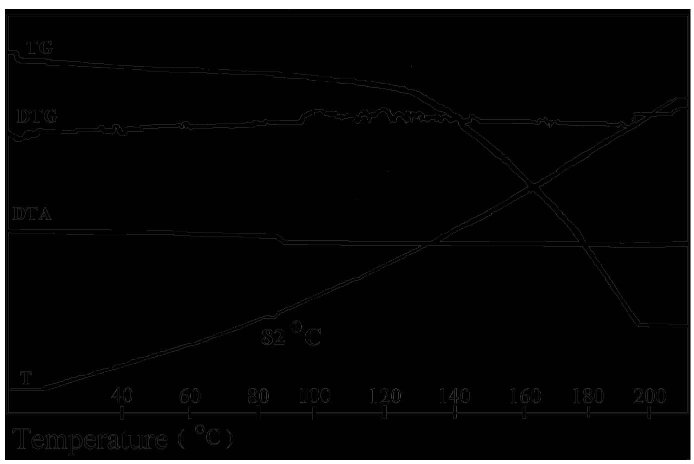
a)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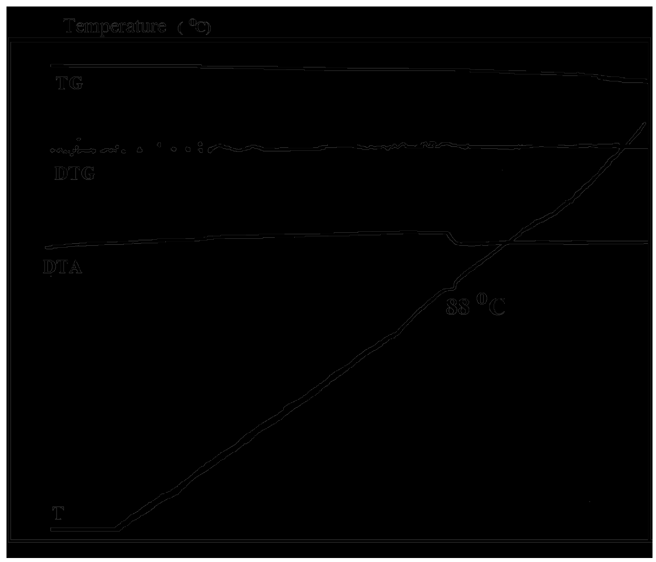
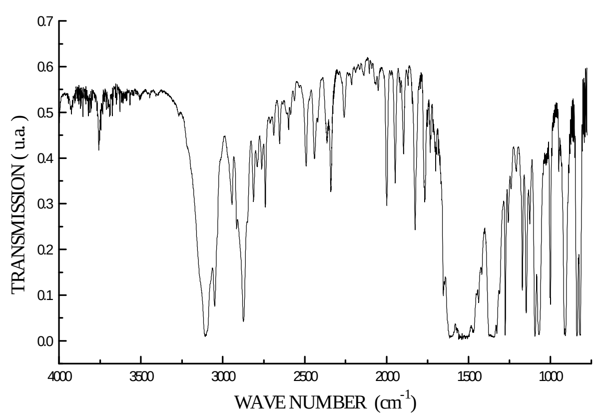
Temperature (°C)

b)

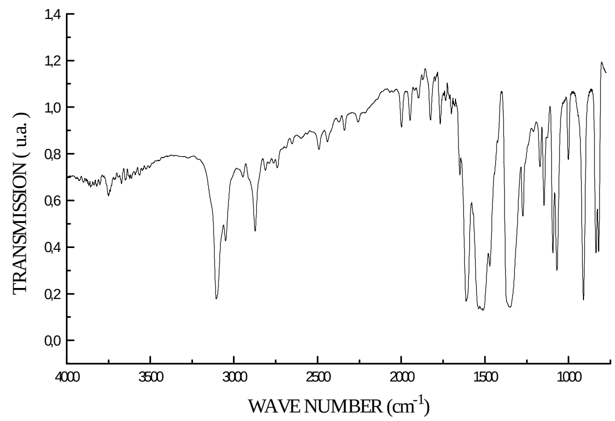


c)

Figure 2 - DTA curves for m-DNB: a) as synthesized; b) chemical purified; c) directional solidification purified.



a)



b)

Figure 3 - FTIR spectra of m-DNB thin films samples of different purity. a) sample from the end of the ingot containing impurity with distribution coefficient k<1; b) sample from the central zone of the ingot of the highest purity.

The main inorganic impurities in meta-dinitrobenzene, obtained by ICP Optical emission spectroscopy, are Si: $1.6x10^{-3}$wt%, Cu: $1.2x10^{-3}$wt%, Mg: $2x10^{-4}$wt%, Fe: $5x10^{-4}$wt%, Al<$2x10^{-4}$wt% but their concentrations are low enough for not disturbing the crystal growth process [2].

4. CONCLUSIONS

This paper presents a comparative study on the effect of the impurities' removal process correlating results obtained using different characterization methods. X Ray diffraction, thermogravimetric and FTIR measurements indicated as major impurities in m-DNB accumulating at the end of the ingot (k<1), ortho dinitrobenzene and benzofurazan. The same methods were utilized for evaluation of the efficiency of the purification stages (chemical purification, vacuum distillation and directional freezing) in reducing the content of organic impurities. Inductively Coupled Plasma Optical Emission Spectroscopy determined the concentration of metallic impurities. The major inorganic impurities were: Si: $1.6x10^{-3}$ (wt%) and Cu: $1.2x10^{-3}$ (wt%). Organic compounds investigated, m-DNB, had purity high enough to be used in crystal growth process.

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