

Study of spectroscopic and thermal characteristics of nonlinear optical molecular crystals based on 4-nitrophenol

Pavlovets I.M.¹, Fokina M.I.¹

¹ITMO University, St. Petersburg 197101, Russia

E-mail: ipavlovets@gmail.com

Abstract. The paper presents the results of study of spectroscopic and thermal characteristics of molecular co-crystals: 2-aminopyridine-4-nitrophenol-4-nitrophenolate (2AP4N) and 2,6-diaminopyridine-4-nitrophenol-4-nitrophenolate (26DAP4N). Crystals were successfully grown by slow evaporation technique. Optical transparency in the region of 190–1100 nm was found to be suitable for applications with cut off wavelengths 420 and 430 nm respectively. Thermogravimetric and differential thermal analysis show good quality and thermal stability for studied crystals. Kurtz and Perry powder technique proves that the crystals are acentric and have significant nonlinear optical response.

1. Introduction

Organic nonlinear optical (NLO) crystals play an important role and provide major benefits to some very important applications, such as laser frequency conversion, electro-optic modulation, frequency mixing and many others [1,2]. Three classes of NLO materials are used today: inorganic crystals (e.g. LiNbO₃), polymers or dendrimers doped with NLO dye molecules (e.g. DR-1, CLD-1), and organic crystals with large NLO coefficients [3,4]. Organic NLO materials have attracted some attention because of the advantages offered by organic systems including high NLO susceptibilities (compare to inorganic compounds), fast response time, relative ease of device processing, etc. [4]. Usually, organic systems with significant NLO properties are the π -electron conjugated chromophores with strong electron donor group on the one end and acceptor on the other [4].

Creation of new efficient second-order NLO materials requires optimization of donor-acceptor chromophores in noncentrosymmetric crystalline lattice or in a polymer matrix [5]. To fulfil this requirement we crystallized two organic chromophores: one acidic (4-nitrophenol) and one basic (2-aminopyridine or 2,6-diaminopyridine). 4-nitrophenol is a classic dipolar NLO chromophore and a donor-acceptor π -system, and presence of the possibility of proton transfer of the phenolic OH group of 4-nitrophenol to various organic bases can result in increasing of its molecular hyperpolarizability [6]. Aminopyridine complexes are well-known series of compounds with good optical properties, thermal stability and suitability for optoelectronics devices [7–10].

We continue our studies in the field of NLO crystals including DAST [11] and different molecular crystals [12–14]. The present work is focused on the spectroscopic and thermal properties of two herein presented organic co-crystals for nonlinear optical applications: 2-aminopyridine-4-nitrophenol-4-nitrophenolate (2AP4N) and 2,6-diaminopyridine-4-nitrophenol-4-nitrophenolate (26DAP4N).



2. Experimental

2.1. Synthesis and crystal growth

To produce and study two herein presented organic compounds the reported synthetic procedure [15] was used as a basis for preparation of 2AP4N and 26DAP4N. Ethanol was used as a solvent.

For the synthesis, an ethanol solution of 4-nitrophenol was added to an ethanol solution of 2-aminopyridine or 2,6-diaminopyridine. Initial reagents have been taken in molar ratio 2:1.

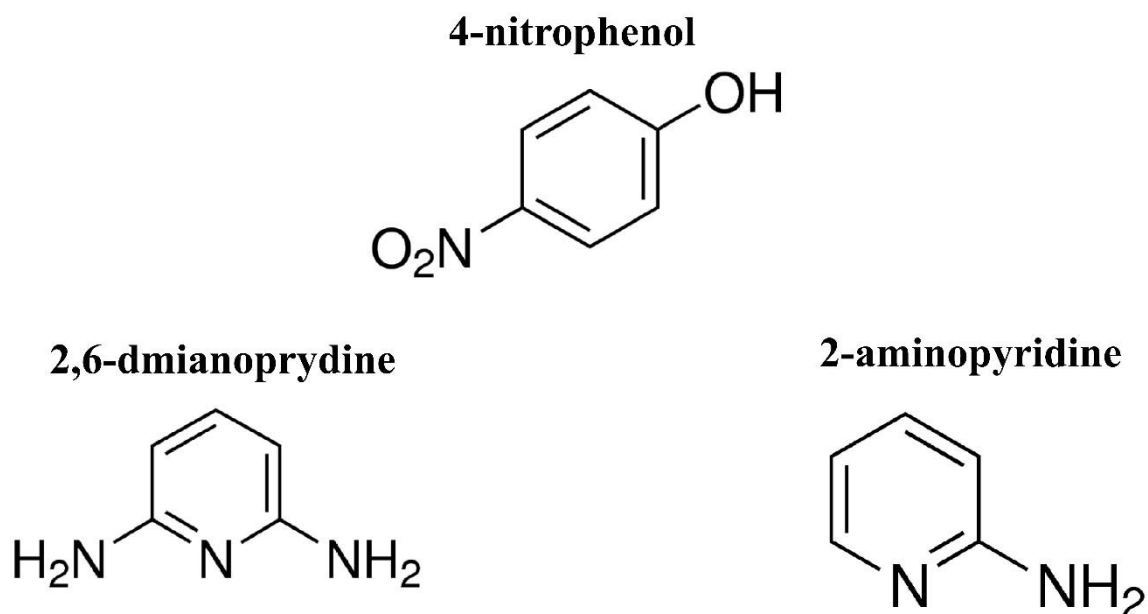


Figure 1. Structural formula of initial reagents

Preparation of 2AP4N: 4-nitrophenol (0.01 M) was dissolved in ethanol (150 ml) and mixed with ethanol solution (50 ml) of 2-aminopyridine (0.005 M).

Preparation of 26DAP4N: 4-nitrophenol (0.01 M) was dissolved in ethanol (150 ml) and mixed with ethanol solution (50 ml) of 2,6-diaminopyridine (0.005 M).

Crystals were grown by slow evaporation technique at a fixed temperature (25 °C). The mixtures of solutions were stirred, filtered, covered with pores filter paper, and placed into the thermostat for slow evaporation of the solvent. After two weeks the solutions were evaporated and the named crystals were successfully grown.

2.2 Instruments for characterization

Thermal characteristics studies were carried out using Thermo Gravimetry/Differential Thermal Analyzer (TG/DTA) HITACHI STA7200. Samples under study were weighted in and aluminium pans with a microprocessor driven temperature controller. TGA and DTA curves of the studied crystals were recorded in nitrogen atmosphere in the range 25–350 °C and are shown in Figure 2. Transmittance spectra of these crystals were recorded in the range 190–1100 nm using Shimadzu-1800 spectrophotometer and the recorded spectra are shown in Figure 3. To confirm the presence of the second-order NLO response, second harmonic generation (SHG) conversion efficiency of the grown crystals were measured by the Kurtz and Perry powder technique [16]. A Q-switched Nd:YAG laser operating on wavelength 1064 nm with 10 ns pulse width and 10 Hz pulse rate was used as a light source. Studied crystals were grounded and sieved in the particle size range between 100 and 160 µm.

SHG was confirmed by the emission of green radiation (532 nm) from the samples and collected by a photodiode with sensitivity zone 420–675 nm.

3. Results and dissuasion

TGA and DTA curves of the grown crystals are shown in Figure 2. According to DTA data, all grown crystal samples have no phase transitions between ambient temperature and melting point. DTA curves of the studied crystal samples show endothermic peaks with maxima at 99 and 149 °C for 2AP4N and 26DAP4N crystals respectively, which recognized as the melting points of these crystals. Second endothermic peaks of both DTA curves is the full evaporation temperatures of the materials, which correlates with the TGA curves.

According to TGA curves (Figure 2, blue lines) there is no weight loss between ambient temperature and the melting points for both of the crystals, which show that the obtained crystals have no inclusion of solvent (which was used for co-crystallization) or other impurities in the crystal lattices. Weight losses start from the melting point and continue up to full evaporation of the materials.

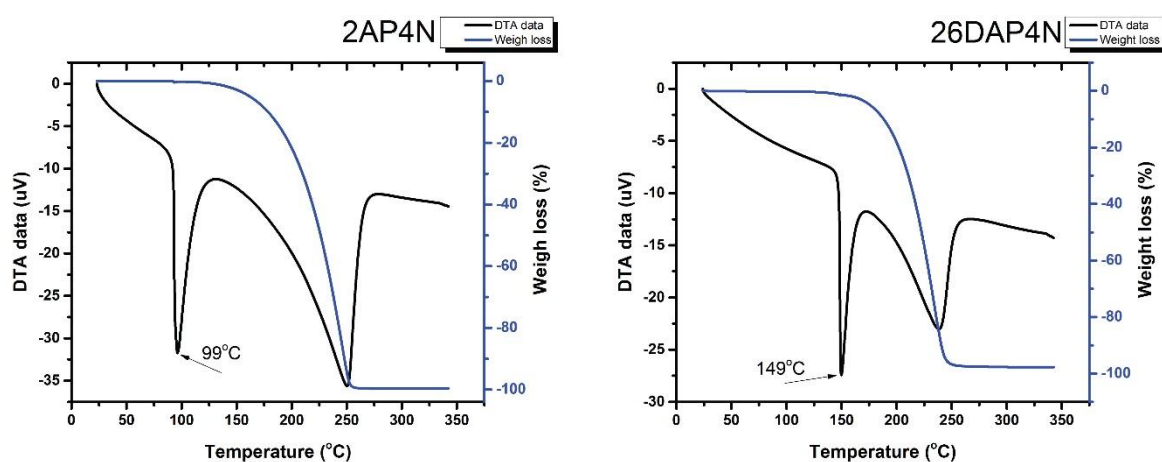


Figure 2. TGA and DTA curves for 2AP4N and 26DAP4N crystals

Transmittance in the visible and near infrared regions of the spectrum is an important parameter which determining the application areas of the material. If the crystals are used for SHG of Nd:YAG laser, the transmittance at the fundamental wavelength (1064 nm) and at the SH wavelength (532 nm) is a necessary parameter.

The obtained transmittance spectra (Figure 3) show that the 2AP4N crystal has wide range of optical transmission of above 80% up to 1100 nm from cut off wavelength (420 nm), and the 26DAP4N crystal has transmission of about 55% up to 1100 nm from cut off wavelength (430 nm). According to these spectra, all the studied crystals have almost the same level of absorption at the fundamental and SH wavelengths of Nd:YAG laser.

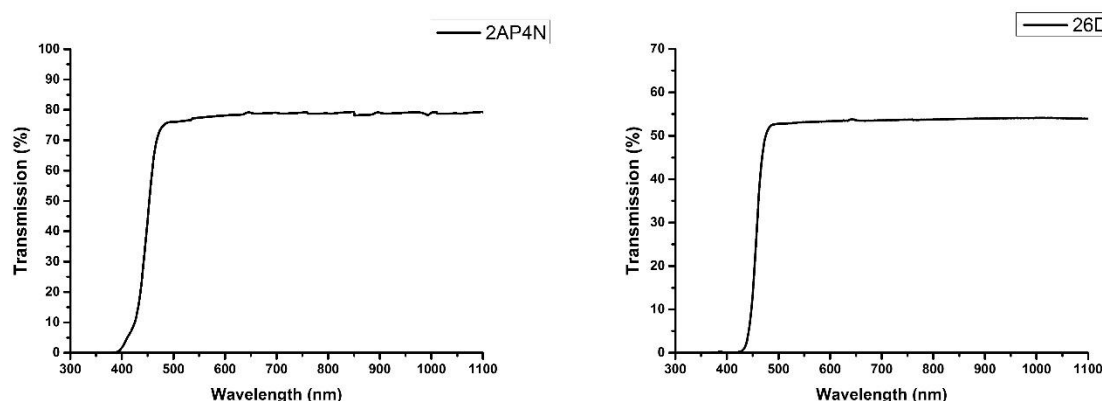


Figure 3. Transmittance spectra of studied crystals

In order to confirm the presence of the second-order NLO response, powder samples of studied crystals were subjected for the Kurtz and Perry powder test [16], which is one of the most effective ways to evaluate the effectiveness of materials for the second harmonic generation. Both the studied samples has shown the presence of a good nonlinear optical response. The relative SHG intensity of 2AP4N crystal was found to be 1.9 times more than that of 26DAP4N crystal with the same particle size range.

4. Conclusion

Good quality and transparent single crystals of 2-aminopyridine-4-nitrophenol-4-nitrophenolate and 2,6-diaminopyridine-4-nitrophenol-4-nitrophenolate were grown successfully by slow evaporation technique with ethanol as a solvent. Obtained results demonstrated that the studied crystals can be used applications below 99 oC. Second harmonic generation studies has shown the presence of significant second-order NLO response. All these properties show that the studied crystals may be promising candidates for the fabrication of NLO devices.

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