Optics and Laser Technology 108 (2018) 450–455

Contents lists available at ScienceDirect

Optics and Laser Technology

journal homepage: www.elsevier.com/locate/optlastec

Full length article

Aminopyridines and 4-nitrophenol cocrystals for terahertz application

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ARTICLE INFO

Article history:
Received 30 December 2017
Received in revised form 26 June 2018
Accepted 14 July 2018

Keywords:
Nonlinear optical materials
Molecular crystals
Terahertz generation
Phase mismatch
Aminopyridine
4-nitrophenol
Co-crystal

ABSTRACT

Co-crystals series of different mono- and diaminopyridines non-centrosymmetric complexes, namely 3,4-diaminopyridine-4-nitrophenol-4-nitrophenolate, 2,6-diaminopyridine-4-nitrophenol-4-nitrophenolate and 2-aminopyridine-4-nitrophenol-4-nitrophenolate were grown by slow solvent evaporation from solution with constant temperature technique. Terahertz absorption and refraction properties of the materials were measured, and the co-crystals were tested as generators of THz pulses under irradiation with 800 nm Ti:Sapphire femtosecond laser. Efficiency of the optical-to-THz conversion was compared to that of ZnTe crystal.

1. Introduction

Within the last ten years, the field of terahertz science and technology has developed dramatically. Enormous amount of new and promising advances in the technology of terahertz generation and detection have been made. Most of successful studies in these scientific areas have been devoted to new materials and technology for terahertz generation and detection development [1]. Optical rectification in electro-optical crystals has been demonstrated as the best technique for generating subpicosecond pulses of electromagnetic radiation in the terahertz (THz) spectral range [2]. Many scientific groups have examined various nonlinear materials for THz emission under optical rectification. These materials include organic salts such as 4-*N*,*N*-dimethylamino-4-*N*-methylstilbazolium tosylate (DAST) [3], inorganic electro-optical materials like $LiTaO_3$, $LiNbO_3$, and semiconductors GaAs, GaSe, InAs, InP, GaP and others [4,5]. DAST co-crystal is one of the most efficient THz rectification material [6]. There are three important requirements for high efficiency of optical-to-terahertz conversion in non-linear optical crystals:

- High non-linear coefficients (susceptibility);
- Low intrinsic terahertz absorption of crystals;
- Phase matching conditions: difference between the group velocity for optical radiation at the central wavelength of the laser and phase velocity for THz radiation should be minimal in a broad frequency range in THz spectral region.

Phase matching is the major factor determining the efficiency of THz pulse generation and the bandwidth of emitted radiation. These conditions also determine the coherence length at desired THz frequency which helps the researcher to choose the optimal thickness of the nonlinear crystal for optimal balance between the amplitude and spectral bandwidth of emission.

Several organic crystals are known for exceptionally efficient optical rectification of femtosecond laser pulses: DAST, DSTMS, OH1, HMQ-TMS [7,8]. The phase matching conditions for these crystals are met for wavelengths of the optical pulse in the near infrared range (usually higher than 1 μm). However, the efficient organic nonlinear crystals for the middle of the operation range of most Ti:Sapphire lasers (near 0.8 μm) are lacking.

Among organic crystals applicable for THz emitting via optical rectification DAST co-crystal is most useful, because of its high thermostability up to 250oC, large EO coefficient and a low dielectric constant (ε = 5.2), giving a rise to a high modulator figure of

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https://doi.org/10.1016/j.optlastec.2018.07.033
0030-3992/

merit [9]. According to experimental data presented in [10], DAST exhibits the second-order NLO susceptibility $\chi^{(2)} = 202 \pm 22$ pm/V at $\lambda = 1318$ nm and the electro-optical figure of merit $n1^3\ r_{11} = (53 \pm 6)$ pm/V at $\lambda = 1313$ nm. Insignificant phase mismatch or even equality between terahertz and infrared (1.06 μm) waves propagation velocity is another advantage of DAST co-crystal. However, very high price for DAST crystals and demand for using the femtosecond lasers with wavelength longer than 1 μm encourage researchers to look for other non-linear organic crystals which would possess high efficiency and good phase matching at 0.8 μm. Besides, as it shown in [11], DAST exist in at least three forms: two crystalline anhydrate forms showing strong nonlinear optical properties and hydrate form which is crystallized in an orange triclinic phase without substantial nonlinear response. Therefore, the presence of water vapor in air can cause the change in DAST morphology leading to loss of nonlinear properties, which is sometimes observed experimentally.

In our work, we study the promising candidates for THz applications: three amionopyridines – 4-nitrophenol based co-crystals, which are not hygroscopic and have high laser damage threshold [12]. For high second order nonlinear susceptibility synthesis of crystalline materials requires to orient donor-acceptor chromophores in non-centrosymmetric manner [13]. To obtain non-centrosymmetric packing, heterocyclic molecules of different aminopyridines were co-crystallized with NLO chromophore 4-nitrophenol (4N). Aminopyridine complexes are well-known series of compounds [14,15] with good optical properties, thermal stability [16] and suitability for optoelectronic devices. 4-Nitrophenol is a classic dipolar NLO chromophore, and the possibility of proton transfer from the OH group of 4-nitrophenol to various organic bases results in increasing of its molecular hyperpolarizability [14,17]. First report on these co-crystals structures was presented by Prakash et al. [14]. Their nonlinear proprieties in the optical range were investigated in our previous the work [18].

One of the co-crystals from this series of aminopyridines was examined in the work [19]. In this study co-crystal 2,6-diaminopyridinium-4-nitrophenolate-4-nitrophenol prepared by same technique was used. Terahertz emission, THz spectra, and refractive index of the co-crystals were measured. The authors claimed the THz emission amplitude comparable to that of ZnTe crystal which encourages for further inspection of co-crystals of this series. However, it was mentioned that shape of crystals was not convenient for such measurements. It influenced on high light dispersion and incorrect measurement of optical absorption spectra, as a sum of optical absorption and dispersion loss, and possible incorrect measurements of terahertz proprieties.

In present research, we continue our previous study of several molecular aminopyridine – 4-nitrophenol co-crystals complexes [18] by using them as generators of broadband THz radiation induced by the femtosecond optical pulses of Ti:Sapphire laser at 800 nm. The results of terahertz measurements of a series of co-crystals of non-centrosymmetric complexes with good crystalline shapes 3,4-diaminopyridine-4-nitrophenol-4-nitrophenolate (34DAP4N), 2,6-diaminopyridine-4-nitrophenol-4-nitrophenolate (26DAP4N) and 2-aminopyridine-4-nitrophenol-4-nitrophenolate (2AP4N) are presented and discussed.

2. Material and methods

2.1. Synthesis and crystal growth

Initial components for crystals: 3,4-diaminopyridine (Aldrich, 54-96-6), 2,6-diaminopyridine (Aldrich, 141-86-6), 2-aminopyridine (Aldrich, 504-29-0), 4-nitrophenol (Aldrich, 100-02-7) are presented in Fig. 1. All of them were commercially available and used without further purification. Crystals were grown by slow solvent evaporation technique at fixed temperature (from 18 till 35 °C, different for each system). This technique is widely used by several groups of scientists [14–16,20,21]. We followed the synthetic procedure of co-crystals production with 4-nitrophenol that was published by Prakash et al. [14]. Ethanol was used as a solvent. For the preparation of the solutions for co-crystallization, the components were dissolved in ethanol and mixed in 2:1 (4-nitrophenol: aminopyridine) molar ratio.

The mixture of solutions was stirred at room temperature for 1 h using magnetic stirrer. Continuous stirring ensured that obtained mixture of solutions is homogeneous. High purification level of synthesized compound was achieved by successive recrystallization of obtained crystals in the same solvent. The solution was filtered by funnel with quartz cells of micron size. A glass vessel with synthesized clear solution was covered with porous filter paper and placed into the thermostat at 25 °C for slow evaporation of the ethanol. After 15–30 days, 50% of solutions were evaporated and the crystals were grown (Fig. 2). Three types of co-crystals of 4-nitrophenol with different aminopyridines were grown successfully with sizes up to centimeters in one dimension for 34DAP4N, 26DAP4N and 2AP4N. According to our previous experience these crystals are not forming polymorphs when crystallized from different solvent. Their molecular and crystal structures are characterized using X-ray diffraction and results are described in detail in our work [16]. Obtained co-crystals, like most organic crystals, are fragile and can be destroyed by mechanical polishing, so the production of single crystals is important.

SHG conversion efficiency of the obtained single crystalline samples was measured by comparative SHG technique presented in our previous work [18]. An estimation of the nonlinear optical coefficient magnitude (d), at 1064 nm, considering the thickness of the samples and the disordering of the crystalline regions that fall into the laser beam, gives values near: 13 pm/V for 34DAP4N, 21 pm/V for 26DAP4N and 39 pm/V for 2AP4N, which allows to consider these crystals as materials with high nonlinear optical parameters. These values of nonlinear coefficients of the co-crystals are quite sufficient for terahertz generation via optical rectification method.

Transparency of the materials in visible, UV and infrared ranges was studied with Shimadzu UV-1800 spectrophotometer in the range 190–1100 nm to show absence of light dispersion by threshold of absorption value near to crystalline absorption edge – 480 nm and high transmittance in transparent area.

For studies of THz transmission properties of the co-crystals we used a terahertz time-domain spectrometer schematically shown in Fig. 3. This spectrometer allows one to study the terahertz absorption and refraction properties of the co-crystals and the spectra of THz radiation, generated in the samples irradiated by femtosecond optical pulses. In this spectrometer, the THz radiation is generated when a femtosecond pulse from a Ti:Sapphire laser (Spectra Physics Tsunami, 797 nm, pulse width 120 fs, 80 MHz repetition rate) irradiates 1 mm thick ⟨1 1 0⟩ ZnTe crystal [22]. THz radiation is collimated and focused into free space using a pair of parabolic mirrors. For spectroscopic measurements, the sample is placed in the THz beam waist. After passing the sample, THz radiation is again collimated and refocused into the detector crystal using two off-axis parabolic mirrors. For detection of THz radiation, we use a 2-mm thick ⟨1 1 0⟩ ZnTe crystal and traditional electro-optical method (Fig. 3). The signal from the balanced detector is sent to lock-in amplifier for increasing the signal-to noise ratio. The pump beam is modulated at frequency 1300 Hz with a chopper, and this frequency is used as reference for the lock-in amplifier.

To study the THz generation in these co-crystals, we replace the ZnTe generator crystal with the sample under study. The energy of the femtosecond pulse has been kept at the same value for