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Manipulating the Refractive Index of THz Generation Crystals

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***Abstract*—BNA and MNA are yellow organic crystals that can efficiently generate terahertz (THz) frequency light when pumped with infrared or 800 nm wavelengths. However, THz generation across a broad range of frequencies could be increased if the phase matching could be improved. In an effort to alter the material refractive index at pump and THz frequencies, we modify the structures of BNA and MNA aiming to improve phase matching ability.**

I. INTRODUCTION

NONLINEAR organic (NLO) crystals are powerful tools to generate high-field, broadband terahertz (THz) light. NLO THz generation crystals like OH-1, DAST, and DSTMS are capable of producing THz field strengths above 1 MV/cm when pumped with infrared (IR) pulses. BNA is a useful NLO crystal when working with titanium-sapphire lasers, producing high-field THz when pumped with 800 nm light [1]. In the past, through a data mining process [2], we developed the NLO crystal PNPA, which has become a new industry standard for THz generation when pumped with infrared (IR) light, generating above 2 MV/cm [3]. We also developed a method for growing MNA, which rivals BNA when pumped with 800 nm light [4].

Various factors must be considered when developing new NLO crystals for THz generation. The crystal must be non-centrosymmetric. Molecular building blocks in organic NLO materials must have a relatively high hyperpolarizability and a crystal-packing order parameter as close to one as possible [2]. The crystals also must be phase-matched, meaning the speed of the pump pulse within the crystal must be similar to the speed of the generated THz pulse. This is achieved by matching the pump group index to the THz refractive index. Good phase matching allows the THz amplitude to continuously grow as the pump pulse passes through the crystal, without detrimental destructive interference that limits the final THz field strength emitted from the NLO crystal.

We altered the refractive index of BNA and MNA THz generation crystals in two ways and characterized the impact on the phase matching and THz generation ability. For MNA, we doped the crystals with zinc, and for BNA, we made small alterations of the BNA molecular structure by substituting different functional groups. Both methods show promise for altering the phase matching properties of these organic NLO crystals.

II. RESULTS

First, we will discuss growing derivatives of BNA and later we will explain doping MNA with zinc.

We created derivatives of the well-known THz generator BNA. In Figure 1 a-d we show BNA and the three BNA derivatives that we grew by attaching different functional groups to the phenol group in BNA. The purple circle in Figure 1a indicates the hydrogen on the BNA phenol group that is replaced with either a methoxy, fluorine, or methyl group creating methoxyl-BNA (Figure 1b), fluoro-BNA (Figure 1c), and methyl-BNA (Figure 1d). All of our BNA derivatives are in the same space group as BNA, with minimal changes to the structure and crystal packing.

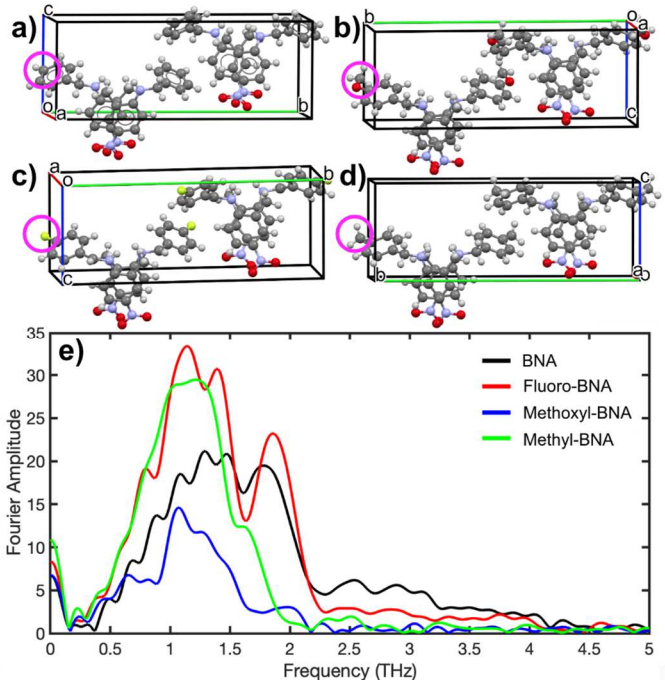

Fig. 1. a) Unit cell of BNA with the replaced hydrogen circled (purple). b) Unit cell of methoxyl-BNA, methoxy group circled in purple. c) Unit cell of fluoro-BNA, fluoro group circled in purple. d) Unit cell of methyl-BNA, methyl group circled in purple. e) THz generation of BNA and the BNA derivatives using an 800 nm pump.

We measured THz generation by pumping with 800 nm, ~100 fs light pulses from our Ti:sapphire laser (Figure 2b). The generated THz is directed through a three-parabolic mirror setup and focused onto an electro-optic sampling crystal which is then probed with an 800 nm pulse. The probe is measured on balanced photodiodes through heterodyne detection.

In Figure 1e, we show the THz generation data for the BNA and the BNA derivatives using an 800 nm pump pulse. The methoxyl-BNA, which has the highest polarizability, generates the lowest amplitude of THz. The quality of the methoxy-BNA crystal was lower than the other crystals, which contributes to its lower THz generation performance. The methyl- and fluoro-BNA both generate higher field THz than the BNA at 800 nm. The fluoro-BNA generated the highest amplitude of THz.

We calculated the hyperpolarizability and order parameters of these four crystals. These can be crucial parameters for determining the THz generation abilities of crystalline

materials. Generally, a crystal is more likely to generate THz well if it has a high polarizability and an order parameter close to 1, which indicates head-to-tail alignment in the crystal structure that will improve THz generation. For BNA, fluoro-BNA, methoxyl-BNA, and methyl-BNA the hyperpolarizability values were 1.92e-29, 2.03e-29, 2.14e-29, and 2.06e-29 esu respectively. For those same crystals we calculated an order parameter of 0.637, 0.640, 0.569, and 0.629 respectively. From these calculations, the highest hyperpolarizability was the methoxyl-BNA, which had a value even higher than that of BNA itself; however, it had the lowest order parameter. The crystal with the highest order parameter and a relatively high hyperpolarizability as well was the fluoro-BNA, which is the only BNA derivative to exceed BNA in both of those categories. The high generation capabilities of fluoro-BNA that we measured were consistent with its high order parameter and hyperpolarizability values. However, replacing the functional group in BNA does not change its structure or space group and the calculated order parameters and hyperpolarizabilities for BNA and its derivatives are relatively similar. This indicates that the difference in generation ability that we see between the crystals is likely due to increasing the phase matching capabilities of the methyl-BNA and fluoro-BNA and not to changes in the crystal packing.

The second experiment we performed was to dope MNA with zinc. We heated MNA in a sand bath, causing it to sublimate onto a cold finger from which we extracted seed crystals. We placed the seed crystals in a saturated solution of MNA dissolved in acetone with 0.1% zinc in solution. Using this process, we grew one large doped MNA crystal, which we divided into three separate smaller doped MNA crystals. Separately using the same method, we grew a second doped MNA crystal. Therefore, we have three doped MNA crystals with the same percentage of zinc incorporated and one crystal doped with a slightly different percentage of zinc. We measured the concentration of zinc in these crystals using inductively coupled mass spectrometry and confirmed that the zinc concentrations were different.

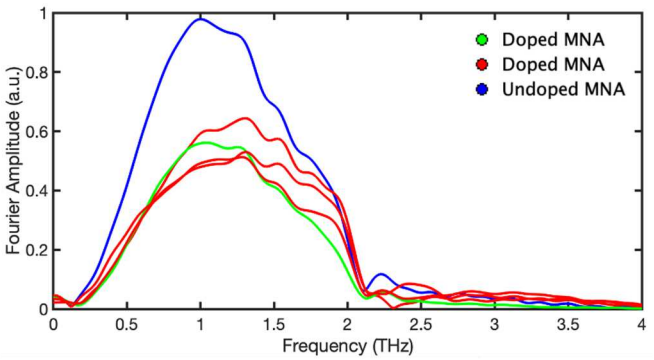

Fig. 2. THz generation with an 800 nm pump for all the doped MNA crystals compared to the undoped MNA.

We used an autocorrelator to measure the group index of these four doped MNA crystals and one undoped MNA crystal at 800 nm. The average group index of the doped MNA was 2.2, while the average group index of the undoped MNA was 2.4. The zinc doping significantly changed the group index compared to the undoped MNA group index, indicating that we have succeeded to change the refractive index of a crystal through doping with a metal.

We measured THz generation of the doped MNA and undoped MNA by pumping with 800 nm light in the same experimental scheme described about for the measurements on BNA derivatives (Figure 2). We observe that the doped MNA crystals output an amplitude ~45% smaller than the amplitude of the undoped MNA. We hypothesize that this is because we have successfully raised the group index of the doped MNA crystals, making the group index farther from the THz refractive index and decreasing phase matching. These results were a very encouraging proof of concept, first indicating through the autocorrelator measurements that we could successfully change the pump group index of a crystal by doping with a metal. Second, the dramatic change in THz output of the doped MNA compared to the undoped MNA shows that we can greatly affect the THz generation properties of crystals through doping.

Overall, it is encouraging that using both of these methods, we were able to alter the THz generation capabilities of the NLO crystals, providing evidence that we are indeed manipulating the refractive indices of MNA and BNA in order to change the phase-matching ability of the crystals.

III. Summary

In summary, we doped MNA and changed the group index of the pump pulses, but doping made the MNA generate less THz. We also added functional groups to BNA to manipulate its refractive index, with preliminary results showing fluoro-BNA produces more THz than BNA when pumped with 800 nm light.

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