Frontiers in Optics + Laser Science (FiO/LS) @ Optica Publishing Group 2022

A New Screening Methodology for THz Generation Crystals

(Enoch) Sin-Hang Ho, Gabriel A. Valdivia-Berroeta, Claire Rader, Natalie K. Green, Daisy J. Ludlow, Paige Petersen, Caitlin Chartrand, Connor Barlow, Stacey J. Smith, David J. Michaelis, Jeremy A. Johnson

Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT, 84602 USA

jjohnson@chem.byu.edu

Abstract: We discover, develop, and test new organic nonlinear optical crystals that produce intense pulses of terahertz radiation through a combination of data mining from Cambridge Structural Database and density functional theory calculations.

1. Introduction

The discovery and design of advanced organic materials with useful properties is essential to the advancement of many fields, including nonlinear optics, catalysis and electron transport. These unique properties are closely related to the molecular building blocks and structure of the materials [1]. In recent decades, aggregating data in material databases and making the data extractable to aid in 1st-principles calculations has greatly enhanced the process of identifying possible candidates for specific uses. Computational methods, such as density functional theory (DFT), enables us to calculate the properties of molecules while material databases can be used to provide required input information for the calculation such as atomic position, molecular bonding, charges of molecules and crystal structure information. The idea that one can easily mine information about known materials for the development of new and extremely useful purposes, rapidly accelerating the discovery of new materials for many applications. This data mining approach is giving rise to new screening methodologies in the rapidly growing field of materials informatics.

Terahertz radiation, with frequencies from 1-10 THz (wavelengths of 300-30 μm), exhibits unique interactions with many materials in ways that differ from other forms of radiation. Many emerging and potentially disruptive applications of THz spectroscopy are taking advantage of these unique interactions, including in chemical recognition, bioimaging and security [2], non-destructive chemical monitoring in industry and food processing, and wireless communication and high-speed computational devices [3]. Of the various methods available for generating THz light, optical rectification of infrared (IR) light with organic nonlinear optical (NLO) crystals is the most efficient method to produce high-intensity THz fields with extremely broad bandwidths [4]. Organic crystals are efficient in optical rectification due to the fact that the organic molecules have high hyperpolarizability and the crystal packing can be easily modified by modifying the molecular building blocks.

In this report we combine data mining of known organic materials from the Cambridge Structural Database (CSD) with DFT calculation of key molecular properties to identify new candidate organic materials for intense terahertz (THz) generation. We then validate our combined data mining and computational approach to materials discovery by synthesizing and fully characterizing new THz generating organic materials.

2. Results

Our initial data mining effort focused on neutral non-centrosymmtric crystals that contain conjugated π-systems and light atoms (lighter than Br). From a starting pool of over 1 million materials in CSD, 15,782 compounds isolated based on our selected criteria. All the resulting compounds were submitted for DFT hyperpolarizability calculations. A crystal packing order parameter, which indicates the degree of optimal packing in a molecular crystal for NLO applications, was calculated for each structure. Out of the candidates, four were synthesized on a large scale and were amenable to large crystal growth, namely PNPA, ZPAN, NMBA and TMOAT.

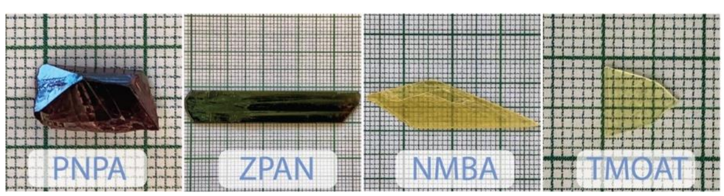

Fig. 1. Large single crystals grown via slow evaporation protocols (square = 1 mm2).

Each of these newly identified crystals generate THz (Fig. 2). In the red crystal category, we compared THz generation from an PNPA and a ZPAN crystal with industry-standard THz generators DAST and OH-1. The THz spectrum of PNPA exceeds that of both OH-1 and DAST, with a spectral peak at 1 THz. In the yellow crystal category, the THz generation of NMBA is very broadband, and it is comparable to that of BNA.

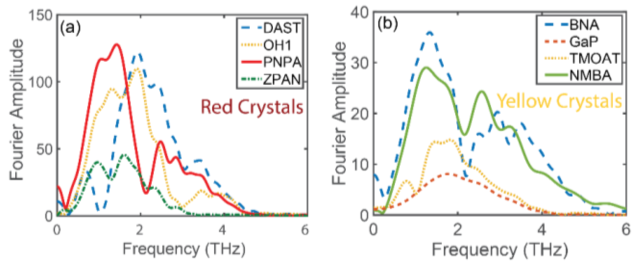

Fig. 2. a) Spectra of red crystals pumped at 1450 nm b) Spectra of yellow crystals and GaP pumped at 1250 nm.

Because of this initial success, we decided to incorporate a more complete model to further assess the THz generation capability of compounds based on both molecular alignment and hyperpolarizability, and expand our improved calculation methods beyond the initial candidate compounds. We calculated the second-order susceptibility ($\chi^{(2)}$) and polarization of the crystals [5]:

$$\chi^{(2)} = \left[d_{IJK}(0\omega;\omega,\omega)\right] = \left[N f_I^{0\omega} f_J^{\omega} f_K^{\omega} \sum_{\substack{s=1 \\ i,j,k}}^{n} cos\big(I,i(s)\big)\, cos\big(J,j(s)\big)\, cos\big(K,k(s)\big)\, \beta_{ijk}(s)\right] \quad (1)$$

$$\begin{bmatrix} P_X \\ P_Y \\ P_Z \end{bmatrix} = 2\epsilon_0\left[d_{IJK}(0\omega;\omega,\omega)\right]\begin{bmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2E_yE_z \\ 2E_xE_z \\ 2E_xE_y \end{bmatrix} \quad (2)$$

In eq. 1, N is density, $f_I^{0\omega}, f_J^{\omega}, f_K^{\omega}$ are Lorentz local-field factors. The summation of the cosine terms account for the conversion between the molecular reference frame (i, j, k) and the crystal reference frame (I, J, K) over all the molecules in a unit cell (n). $\beta_{ijk}(s)$ is molecular hyperpolarizability tensor components for each molecule.

In eq. 2, the P_i terms represent the crystal polarizations and the E_i terms account for the polarization of input light.

We calculated the relative maximum polarization values for all main faces and for all the potential crystal THz generating candidates. Table 1 shows the maximum polarization values for our previously test THz generation crystals. The relative order of the calculated polarization values for the red crystals are consistent to the relative THz generation performance shown in fig. 2a. For the yellow crystal side, the relative order is also consistent except for the BNA crystal. This indicates the calculated polarization values can potentially account for THz generation capability.

Table 1. Polarization values for tested crystals and some potential candidates

Red Crystal	P_{max}	Yellow Crystal	P_{max}	New Crystal (CSD ID)	P_{max}
DAST	37.39	BNA	4.36	YISCIM	114.39
OH1	17.93	NMBA	15.03	BIQSOJ	81.60
PNPA	71.21	TMOAT	8.03	QIRCID	59.24
ZPAN	13.16			WIDXAK	37.42

3. Conclusion

Our combination approach of data mining and DFT calculation enables the rapid identification of new organic nonlinear optical material for intense THz generation. This approach is not limited in the THz field, and it is also highly applicable to other fields of material discovery and development.

4. References

[1] Varghese, S.; Das, S., Role of Molecular Packing in Determining Solid-State Optical Properties of π-Conjugated Materials. The Journal of Physical Chemistry Letters 2011, 2 (8), 863-873..

[2] W. L. Chan, J. Deibel, and D. M. Mittleman. Imaging with terahertz radiation. Reports on Progress in Physics 70, 1325 (2007).

[3] I. F. Akyildiz, J. M. Jornet, and C. Han. Terahertz band: Next frontier for wireless communications. Physical Communication 12, 16 (2014).

[4] F. D. J. Brunner, O. P. Kwon, S.-J. Kwon, M. Jazbinšek, A. Schneider, and P. Günter. A hydrogen-bonded organic nonlinear optical crystal for high-efficiency terahertz generation and detection. Optics Express 16, 16496 (2008).

[5] J. Zyss; J. L. Oudar. Relations between microscopic and macroscopic lowest-order optical nonlinearities of molecular crystals with one- or two-dimensional units. *Physical Review A 1982, 26* (4), 2028-2048.