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DAST crystal based terahertz generation and recording of time resolved photoacoustic spectra of N_2O gas at 0.5 and 1.5 THz bands

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ABSTRACT

We report the THz generation using optical rectification process in an indigenously grown organic salt 4-N, *N*-dimethylamino-4′-N′-methyl-stilbazoliumtoyslate (DAST). A 60 fs, 1 kHz optical parametric amplifier, tunable between 0.8 and 1.6 μm range was employed to generate THz radiation. It is observed that the THz signal is accompanied with weak second harmonic signal of pump wavelength. The conversion efficiency (η) of generated THz is 0.0161%. The radiation generated from DAST crystal is only THz signal, which is confirmed theoretically by choosing the crystal thickness is equivalent to be its optimum coherence length. In addition, we have selected two rotational lines i.e. $J = 19$, 58 of pure N_2O gas by using 0.5 and 1.5 THz band pass filters for recording the time resolved photoacoustic (PA) spectra at 1 atm pressure for the first time.

1. Introduction

In recent years, the generation and detection of wide band terahertz (THz) radiation using optical techniques immerged as a new non-destructive tool for spectroscopic application. Moreover, it has potential use in characterization of proteins, pharmaceuticals, explosives and narcotic drugs etc. [1–5]. The generation of tunable THz radiation is achieved by the means of different optical processes such as photo conductive (PC) antennas, electro optic (E-O) sampling, difference frequency generation (DFG) and optical rectification (OR) etc. [6–13]. The organic crystal: 4-N, *N*-dimethylamino-4′-N′-methyl-stilbazoliumtoyslate (DAST) based terahertz generation using different nonlinear optical process and its applications in various fields are reported by several research groups [14–16]. The OR is one of the effective techniques for the generation of powerful THz signal using ultrashort pulses. In the present case, we have generated the terahertz radiation from DAST crystal using optical parametric amplifier pulses tunable between 0.8 and 1.6 μm, range. Enhancement of THz signal in OR process can be achieved by matching the refractive index of generated THz radiation and corresponding group index of incident optical pump beam [17]. The phase velocity of THz and the group velocity of the optical pump beam have closer values due to low dielectric constant of DAST crystal [18]. Therefore, this can generate high power THz radiation, which is further used for the spectroscopic applications.

The second order nonlinear coupling coefficient (d_{eff}) of 4-N, *N*-dimethylamino-4′-N′-methyl-stilbazoliumtoyslate (DAST) is much higher than other well-known nonlinear crystals such as ZnTe, GaSe, CdTe [19,20]. Moreover, it has good transparence between mid to far-infrared wavelength range [21]. We report the generation of efficient THz signal from indigenously grown organic nonlinear crystal DAST, which is grown along the direction of (001) plane. It belongs to monoclinic space group *Cc*, point group *m*, with four molecular units for unit cell [22,23]. It is a positive biaxial crystal, which has high nonlinearity coefficient and broad transmission between 0.8 μm to THz range. Therefore, DAST crystal is treated as one of the promising candidate for generating wide band THz radiation using OR process [24–27].

Efficient THz radiation is generated by selecting suitable wavelengths in the near IR region where d_{eff} of the crystal has maximum value. Bosshard et al. reported the d_{eff} values of DAST crystal using Marker-Fringe experiment [28]. The d_{eff} values at 1.318 μm are $d_{111} = 1010 \pm 110$, $d_{122} = 96 \pm 9$ and $d_{212} = 53 \pm 12$ pm/V, while for 1.542 μm it has $d_{111} = 290 \pm 15$, $d_{122} = 41 \pm 3$ and $d_{212} = 25 \pm 3$ pm/V, respectively. DAST is a positive biaxial crystal and its refractive

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indices are of the order of $n_x > n_y > n_z$. The principal plane XY behave like a positive uniaxial crystal while YZ plane behaves like a negative uniaxial crystal. In case of OR process the extraordinary polarization is selected for pump beam, therefore the generated signal i.e. THz or second harmonic wavelengths are also extra ordinary polarized. The refractive indices of pump and generated wavelengths in XY principal plane are $n^e_{xy}(\lambda_p)$ and $n^e_{xy}(\lambda_{THz})$ respectively. The value of $n^e_{xy}(\lambda_{i=p,THz})$ is calculated using following expression for biaxial crystals,

$$n^e_{xy}(\lambda_i) = \left(\frac{\cos^2(\varphi)}{n_y^2(\lambda_i)} + \frac{\sin^2(\varphi)}{n_x^2(\lambda_i)}\right)^{-\frac{1}{2}} \tag{1}$$

φ is the phase matching angle. The refractive index of DAST crystal at different wavelengths are calculated using following sellmeier equation [29,30].

$$n^2(\lambda) = n_o^2 + \frac{q\lambda_o^2}{\lambda^2 - \lambda_o^2} \tag{2}$$

where, λ is in μm. The values of n_o, q and λ_o parameter are selected along the X,Y, and Z-axis and listed in the Table 1.

Nitrous oxide (N_2O), commonly known as laughing gas is one of the green house molecule. It can be used as an oxidizer in a rocket motor. Robert Goddard proposed N_2O and gasoline as possible propellants for a liquid-fuelled rocket [31]. Plyler et al. reported the frequencies of the vibration-rotation spectrum of N_2O in the range of 4.405–5.464 μm [32]. Palik et al. presented the pure rotational spectra of N_2O between 100 and 600 Microns [33]. Mittleman et al. demonstrated the detection and identification of polar gases and gas mixtures based on the technique of terahertz time-domain spectroscopy [34]. In the present paper, the generated terahertz radiation from DAST crystal is used to record the time resolved photoacoustic (PA) spectra of N_2O at 0.5 and 1.5 THz band pass filters (BPF) to excite the $J = 19$ and 58 pure rotational lines of N_2O. Earlier, the same band pass filters were utilized to design of THz spectrophotometer using LT-GaAs photoconductive antennas, pyroelectric detector [35].

2. Experimental details

2.1. Crystal growth process

The DAST (001) was successfully synthesized in the laboratory by adding the reactants 4-picoline, methyl 4-toluenesulphonate in equimolar ratio and using piperidine as a catalyst. The synthesized starting material was then purified several times by re-crystallization process before proceeding for the growth of the crystal with methanol as solvent. The temperature of the bath (equipped with a controlled accuracy ± 0.01 °C) was kept at 30 °C at which the concentration of the solution was about 19.8 g/l. Later the temperature of the solution was increased to 40 °C for complete dissolution and it was kept at this temperature for about 5 h. Subsequently, the temperature of the solution was slowly lowered to 30 °C with a cooling rate of 0.10 °C/h. The growth was performed by isothermal slow evaporation technique at 30 °C. Transparent single crystals of DAST were harvested after a period of about 10 days. A typical DAST crystal (with a dimension of 3 × 3 × 0.28 mm³) thus grown in the laboratory is shown in Fig. 1.

Table 1
Values of n_o, q and λ_o.

	n_x	n_y	n_z
n_o	2.078	1.585	1.565
q	1.645	0.469	0.234
λ_o(μm)	0.533	0.504	0.501

2.2. Experimental layout for THz generation and detection

The DAST crystal was then studied for its THz generation efficiency. The experimental layout employed for this study is shown in Fig. 2. The required tunability of the pump wavelength was obtained from an optical parametric amplifier (TOPAS-C, Coherent). The input wavelength for OPA was supplied from regenerative amplifier, which provides an output wavelength of 800 nm, pulse duration 40 fs and repetition rate 1 kHz. The tunable optical pump radiation obtained between 0.8 and 1.6 μm was vertically polarized and separated out from their corresponding idler and residual second harmonics using suitable wavelength separators. The tunable pump beam was directed to be incident on a 0.28 mm thick DAST crystal for generating the THz signal and its second harmonics. A Teflon sheet and silicon lens of thickness of 2 and 10 mm, respectively were used as filters for residual incident unconverted and SH signals. The power of generated THz signal was detected by employing a pyroelectric detector (Gentec) which was placed 5.0 cm away from the crystal whereas second harmonic signal was detected in transmission mode using USB 4000 Spectrometer (Endor), which can detect signal between 200 and 1100 nm range. The optical chopper is used to modulate the pump pulses at the rate 25.3 Hz, which acts as reference for pyroelectric detector (PED). The modulated pump beam was allowed to be incident on the DAST crystal. The generated THz signal was detected with the help of a pyro-electric head (sensor) connected to a T-Rad system that consists of pre amplifier, lock-in-amplifier, and used for the signal processing. Finally, the output of the T-Rad was fed to the personal computer (PC) for monitoring the power of the generated THz signal.

2.3. Photoacoustic spectroscopy arrangements

The PA spectrum of N_2O was recorded using a cylindrical resonator type PA cell of internal radius (R) of 7 mm and length (L) of 6.5 cm made of stainless steel. A Teflon, 25 mm diameter sheets and 1 mm thickness were used as a window of the PA cell. A Pre-polarized microphone (BSWA, China) of responsivity 50 mV/Pa was used to detect the generated acoustic signal. The output signal of the microphone was fed to a preamplifier, which was coupled to 200 MHz oscilloscope (Tektronix, U.S.A.). A silicon plate of 50 mm

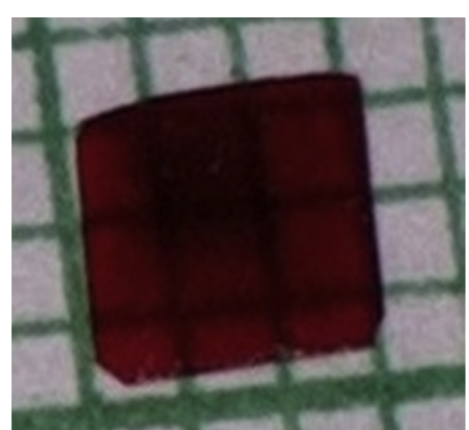

Fig. 1. The picture of DAST crystal (001).