Current Applied Physics 14 (2014) 403–406

Contents lists available at ScienceDirect

Current Applied Physics

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

Characteristics of efficient few-cycle terahertz radiation generated in as-grown nonlinear organic single crystals

Bong Joo Kang [a], In Hyung Baek [a], Jae-Hyeok Jeong [b], Ji-Soo Kim [b], Seung-Heon Lee [b], O-Pil Kwon [b,*], Fabian Rotermund [a,*]

[a] Division of Energy Systems Research and Department of Physics, Ajou University, Suwon 443-749, Republic of Korea
[b] Department of Molecular Science and Technology, Ajou University, Suwon 443-749, Republic of Korea

ARTICLE INFO

Article history:
Received 25 November 2013
Accepted 17 December 2013
Available online 2 January 2014

Keywords:
Terahertz radiation
Nonlinear optics
Optical rectification
Organic crystals

ABSTRACT

We investigated efficient terahertz wave generation by optical rectification in as-grown nonlinear organic single crystal HMQ-T (2-(4-hydroxy-3-methoxystyryl)-1-methylquinolinium 4-methylbenzene sulfonate). Optimal thickness of crystals directly available by a slow cooling method in methanol solution enabled us to achieve high-field few-cycle THz waves at 800-nm pumping. With 95-mW pumping at 1-kHz repetition rate, an optical-to-THz conversion efficiency of 2.7×10^{-4} was achieved and the THz electric field strength, measured by electro-optic sampling, was as high as 110.1 kV/cm. Such an efficient THz source based on as-grown HMQ-T crystals can be used for investigation of various nonlinear phenomena in the THz spectral region.

Published by Elsevier B.V.

1. Introduction

Terahertz (THz) wave, which lies in the frequency range between the infrared and microwave, has attracted a great attention as a new coherent light tool for scientific and industrial applications due to its unique transparency in most dielectric materials without damage and the fingerprinting capability of specific molecular motions [1–3]. As ultrafast THz phenomena came up with interesting subjects of THz technology, intense THz pulses with broad spectra are required for various investigations [4–7]. Nowadays, several techniques, such as electric-field carrier acceleration in semiconductors or photoconductive switch and nonlinear optical processes such as optical rectification (OR) and difference-frequency generation (DFG) in nonlinear materials, have been developed for generation of ultrafast broadband THz waves and used for various THz researches and applications [8–10]. Optical rectification, often used for efficient THz wave generation [11], is a particular case of DFG between two own spectral components under the irradiation of broadband laser pulses with a duration less than 1 ps [12]. In addition to well-known inorganic nonlinear optical crystals such as GaAs and ZnTe applicable as THz emitters, organic electro-optic crystals exhibiting large macroscopic nonlinearity, fast response time, and low dielectric constant have attracted increasing interests for efficient THz wave generation [13–15]. Several parameters such as molecular orientational order parameter, microscopic and macroscopic optical nonlinearity, absorption and transmission characteristics, phase matching characteristics, and thickness controllability of crystals influence to efficiency of the generated THz waves and their spectrum [16,17]. Commonly in phase-matched nonlinear frequency conversion processes, the dispersion control is one of the critical factors in addition to large second-order nonlinearity, since the group velocity (GV) mismatch between the optical pump and the newly emerging THz waves propagating within the medium leads to a temporal walk-off and decreases the conversion efficiency substantially [18–20]. It is therefore essential to find an optimal crystal thickness, which depends on wavelength-dependent refractive index and material dispersion, for efficient THz wave generation.

In our previous report [21], a novel nonlinear organic single crystal, an acentric quinolinium derivative HMQ-T (2-(4-hydroxy-3-methoxystyryl)-1-methylquinolinium 4-methylbenzenesulfonate), was introduced as a potential candidate as THz emitter for the first time. It exhibited a large macroscopic optical nonlinearity and a nearly ideal molecular orientational order parameter of $\cos^3(\theta_P) = 0.92$, close to the perfectly ordered value of 1.0, where the molecular-ordering angle θ_P denotes the angle between the main charge transfer axis of the crystal and the maximal first-order hyperpolarizability of the

* Corresponding authors.
E-mail addresses: opilkwon@ajou.ac.kr (O-P. Kwon), rotermun@ajou.ac.kr (F. Rotermund).

1567-1739/$ – see front matter Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.cap.2013.12.023

molecules. This value is larger than that of the well-kwon non-ionic organic crystal OH1 (2-(3-(4-hydroxystyryl)-5,5-dimethylcyclohex-2-enylidene)malononitrile) ($\cos^3(\theta_P) = 0.69$) and that of the ionic organic crystal DAST (*N*,*N*-dimethylamino-*N*′-methyl-stilbazolium *p*-toluenesulfonate) ($\cos^3(\theta_P) = 0.83$) [22–24]. Due to high molecular orientational order, the magnitude of the macroscopic optical nonlinearity, given by $|\beta_{III}^{eff}|$, of HMQ-T is 155×10^{-30} esu, is comparable to that of DAST (161×10^{-30} esu) and larger than that of OH1 (63×10^{-30} esu) [22–24]. HMQ-T crystal is well transparent in the near-infrared (NIR) and visible spectral range down to 530 nm and phase-matchable at the technologically important wavelength near 800 nm. In addition, as-grown HMQ-T crystals from solution can be directly employed for THz wave generation without any additional treatments such as polishing and cutting. It should be noted that other common organic crystals applicable as THz emitters mostly need additional treatments for obtaining sufficiently high crystal quality for experiments and the thickness control is often very difficult. In the sense, it is very promising to investigate systematically the characteristics of generated THz waves including efficiency and spectral bandwidth in dependence on the thickness of as-grown HMQ-T crystals.

2. Experimental

In this work, a Ti:sapphire regenerative amplifier (Spitfire Ace, Spectra Physics), delivering 100-fs pulses at 1 kHz with a maximum average power of 4 W at the center wavelength of 800 nm, was used as pump source. Output beam was divided in two parts by using a beam splitter. The major portion of the beam was used to pump HMQ-T for THz generation and the minor portion served as the probe beam for electro-optic (EO) sampling. The experiment was performed at room temperature with dry air purging. Prior to pump HMQ-T for THz wave generation, the beam was collimated by the combination of a collimator and an aperture down to a diameter of 1 mm, which is smaller than the input and output faces of the crystal used. The incident pump power was varied up to 95 mW, corresponding to a single pulse energy of 95 μJ, in the present experiment.

HMQ-T crystals with different thicknesses were directly grown by a slow cooling method in methanol solution. In the beginning, seeds of crystal were first created spontaneously and the crystals were subsequently grown during few days. By variation of growth conditions such as cooling rate, saturation temperature, and volume of solution, HMQ-T crystals with different sizes and thicknesses were obtained. The as-grown HMQ-T crystals exhibiting excellent surface properties were used without polishing for experiments. To find out an optimal thickness of the HMQ-T crystal for efficient THz wave generation by GV matching, seven as-grown samples with the (010) surface were available. The size of the crystal face typically ranged from 1.2 to 3.5 mm and the crystal thickness along the crystallographic *b*-axis, i.e. the propagation direction, was measured to be 0.40, 0.54, 0.58, 0.67, 0.76, 0.85, and 1.26 mm, respectively. The polarization of the incident pump beam nearly coincides with the polar axis of the crystal, leading to the best phase matching condition and delivering maximum THz output.

3. Results and discussion

As depicted in Fig. 1(a), temporal characteristics of the THz waves generated in HMQ-T crystals of different thicknesses were recorded by EO sampling in GaP and the corresponding spectra were obtained by fast Fourier transform (FFT) of the time traces of the generated THz electric fields (inset). The upper cut-off frequency, defined as the frequency in the high frequency region at which the THz electric field amplitude $E_{THz}(\nu)$ becomes larger than the average noise level (1.0 in arbitrary units), is illustrated by the dotted horizontal line in Fig. 1(a) inset. The THz signal $\Delta I/I$ measured by balanced photo-detectors was calibrated to THz electric field amplitude E_{THz} with the relation $E_{THz} = [\sin^{-1}(\Delta I/I)\lambda_0]/[2\pi n_0^3 r_{41} t_{GaP} t_{Si} L]$, where the refractive index of GaP is $n_0 = 3.2$, the EO coefficient $r_{41} = 0.88$ pm/V, the thickness $L = 300$ μm. The Fresnel transmission coefficient of GaP is $t_{GaP} = 0.46$ and $t_{Si} = 0.52$ for the Si wafer used as filter [25–27]. Fig. 1(b) shows the thickness-dependent time traces of the generated THz electric fields and the corresponding cut-off frequency at the upper limit of THz spectrum. As expected, the generated THz electric field strength was strongly influenced by material dispersion in different thicknesses. This caused the temporal walk-off between the pump and THz waves. The highest peak THz electric field of 110.1 kV/cm was generated in a 0.58-mm-thick HMQ-T crystal, whereas the broadest spectrum was achieved in a slightly thicker (0.67 mm) sample. The amplitude of the THz electric field and the spectral bandwidth increased with increase of the crystal thickness, so far as the thickness did not exceed the walk-off length. When the crystal became thicker than the walk-off or coherence length, the conversion efficiency decreased remarkably due to GV mismatch and the spectrum became narrower. For crystal thickness of >0.85 mm, the optical pump and the generated THz waves were temporally separated and hence, optical-to-THz conversion was strongly suppressed. From the results, the optimum crystal thickness, which is comparable to the walk-off length, seems to be ~0.6 mm. Although

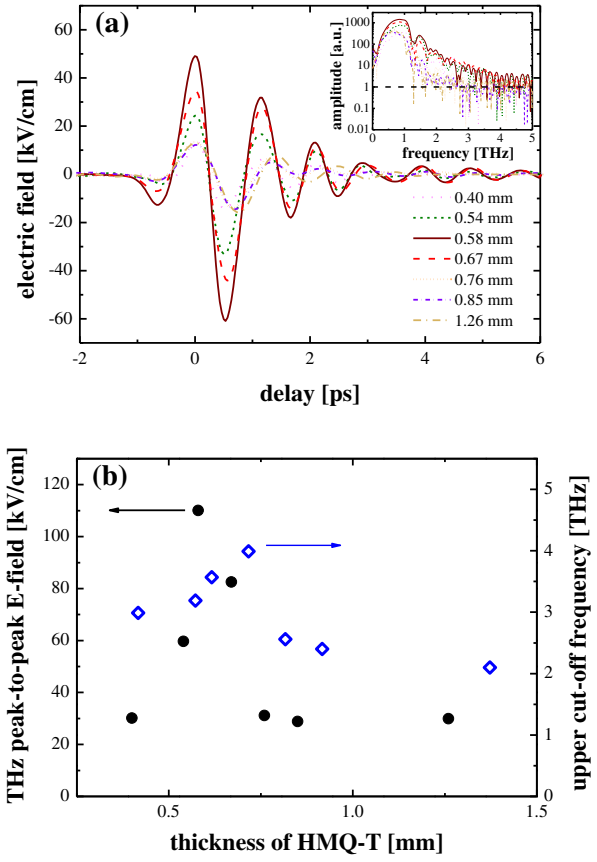

Fig. 1. THz wave generation in as-grown HMQ-T crystals of different thicknesses with pumping at 800 nm and incident average power of 95 mW. (a) Measured time-domain THz electric field $E_{THz}(t)$. The inset shows the corresponding spectra $E_{THz}(\nu)$ in logarithmic scale. (b) The peak-to-peak electric field strength of $E_{THz}(t)$ and the upper cut-off frequency.