Generation of Widely Tunable Terahertz Waves by Difference-Frequency Generation Using a Configurationally Locked Polyene 2-[3-(4-Hydroxystyryl)-5, 5-Dimethylcyclohex-2-Enylidene] Malononitrile Crystal

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Abstract: We generated widely tunable terahertz (THz) waves using difference-frequency generation (DFG) in a configurationally locked polyene (CLP) 2-[3-(4-hydroxystyryl)- 5, 5-dimethylcyclohex-2-enylidene]malononitrile (OH1) crystal. The two waves generated by a KTiOPO4 (KTP) optical parametric oscillator (OPO) were used to pump the OH1 crystal. The maximum output energy of the THz wave was 604 pJ/pulse. Widely tunable THz waves were successfully generated from 0.5 to 10 *THz* by using difference-frequency generation source.

Keywords: Nonlinear optical materials, Difference-frequency generation, OH1 crystal

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1. Introduction

A number of dielectric materials have modest permittivity and fingerprint spectra in the terahertz (THz) wave region. Accordingly, applications to various fields, including physics, chemistry, biology, medicine, and security, are currently anticipated [1, 2]. It is necessary to develop a widely tunable high-power THz wave source and a highly sensitive detector in order to realize these applications. A nonlinear optical material with a large nonlinear optical coefficient is essential for the development of a widely tunable high-power THz wave source, and material with low permittivity is desirable for generating THz waves [3]. In this regard, organic nonlinear optical crystals are promising materials, capable of generating high-power THz waves. In particular, a 4-N, N-dimethylamino-4'-N'-methyl-4-stilbazolium tosylate (DAST) crystal has a large second-order nonlinear optical constant (d_{11} = 230 *pm/V*) and low permittivity, and waves in the 1.5 to 37 THz range have been produced by using difference-frequency generation (DFG) with it [4, 5]. The refractive indices of the DAST crystal in the optical region and the THz region are almost identical. For this reason, collinear DFG phase matching of type 0 (parallel polarization of all waves in nonlinear wavelength conversion) can be achieved. In addition, the melting point and hardness of the DAST crystal are high, since ionic bonds provide the predominant intermolecular force. However, a transverse optical phonon originating from the ionic bonds leads to an absorption band around 1.1 THz [6]. Recently, Kwon et al. used THz time-domain spectroscopy (THz-TDS) to generate THz waves in the 0 to 4 *THz* range with a CLP OH1 crystal [7, 8]. The crystal structure of OH1 has orthorhombic space group symmetry Pna21 and point group symmetry mm2 [9]. OH1 crystals have low absorption in the low-frequency region, and offer the possibility of wideband THz wave generation. Moreover, OH1 has large second-order nonlinear susceptibilities (d_{33} = 120 *pm/V* at 1.9 μm).

2. Experimental Methods

OH1 crystals were grown by seed-crystal and large-crystal growth processes. These processes were carried out in a polytetrafluoro-ethylene (PTFE) vessel. The seed crystals were grown by spontaneous nucleation, and the large crystals were grown by slow cooling. A saturated solution was prepared in accordance with the solubility curve of an OH1/methanol system [10]. A supersaturated solution at 43°C was used to grow an OH1 seed crystal. The solution was obtained by adding 1.5 *g* of OH1 to 40 *g* of methanol in the PTFE vessel, and was stirred for more than 10 hours at 55°C in an incubator. It was then filtered to remove impurities and maintained at 55°C. Next, the OH1 solution was cooled to 32°C and left for 3 days in the incubator. Following this, the OH1 crystal deposits were collected, and the surface of the OH1 seed crystal was washed in methanol for about 10 seconds using a glass dish. Some OH1 seed crystals of the thickness about 0.1 *mm* were obtained.

A large OH1 crystal was then grown by placing the OH1 seed crystal on the bottom of the PTFE vessel in another supersaturated solution at 42°C. This solution was obtained by adding 2.9 *g* of OH1 to 80 *g* of methanol in the PTFE vessel, and was stirred for more than 10 hours at 55°C in an incubator. It was filtered to remove impurities and maintained at 55°C. Next, the dissolved solution was cooled to 42°C in the incubator. The OH1 seed crystal was then placed in the PTFE vessel, and, to melt the crystal surface, it was left for about 20 minutes in the incubator. Afterwards, OH1 was grown at a cooling rate of 1°C/day. The growth period was 12 days. The resulting some OH1 crystals were collected with PTFE tweezers. The surface of the OH1 crystal was washed in methanol for about 10 seconds using a glass dish. The thicknesses of the large OH1 crystals were 0.25, 0.32, 0.40, 0.63, 0.85, and 1.05 *mm*.

The experimental setup for the OH1 difference-frequency generation (OH1-DFG) source is shown in Fig. 1. A dual-wavelength pumping beams were generated by a KTiOPO4 (KTP) optical parametric oscillator (OPO) [5]. The pulse duration, pulse energy, repetition rate, and tunable range of the KTP-OPO were 15 *ns*, 0.4 *mJ*, 50 *Hz*, and 1208 to 1544 *nm*, respectively. The dual-wavelength pumping beams were focused on the OH1 crystal using a lens with a focal length of 100 mm. The line width of the KTP-OPO output was approximately 100 *GHz*. The pumping-wave beam diameter of the two wavelengths on the crystal surface was 200 *μm*. The OH1 crystal was placed beyond the focal length of the lens. The polarization of the input optical waves was parallel to the c-axis of the OH1 crystal. At that time, the power density of the pumping-wave beam was about 100 MW/cm^2.

The THz wave generated with the OH1 crystal was converged using two parabolic mirrors and detected using a liquid-helium-cooled Si-bolometer. A pulse energy of about 100 *pJ/pulse* corresponded to a Si-bolometer voltage output of 1 *V* when the repetition rate was less than 200 *Hz*. The thickness of the OH1 crystal was 0.32 *mm*. The two wavelengths of the KTP-OPO output beams passing through the OH1 crystal were cut using a black polyethylene (BPE) filter. The signal from the detector was transmitted to a computer via an A/D converter, and the THz-wave output spectrum was measured for fixed pump wavelength of λ_1 = 1265 *nm*. The THz frequency was held between 0.1 and 12 *THz* using a Galvano scanner. The resolution of the measured THz spectrum was 100 *GHz*. The resulting THz wave spectrum is shown in Fig. 2. The THz waves were generated over an extremely wideband range of 0.5 to 10 *THz*, without a strong dip at approximately 1.1 *THz*. The dip at 8 *THz* originated from the transmission characteristics

of a filter inside the Si-bolometer. At frequencies above 10 *THz*, the detection efficiency of the Si-bolometer decreased, resulting in the low power observed at higher frequencies.

The resulting THz wave output spectrum by dependence for thickness of OH1 crystals is shown in Fig. 3. The thicknesses of the OH1 crystals were 0.25, 0.40, 0.63, 0.85, and 1.05 *mm*. The THz-wave output spectrum was measured for fixed pump wavelength of λ_1 = 1265 *nm*. The resolution of the measured THz spectrum was 100 *GHz*. The power density of the pumping-wave beam was about 50 MW/cm^2. In addition, the THz-wave output increased with increasing OH1 crystal thickness, and the maximum output energy of the THz wave when the OH1 crystal of the thickness of 1.05 *mm* was used was 604 *pJ/pulse* when the THz frequency was 2.1 *THz*.

3. Conclusion

Widely tunable THz waves were generated using DFG with a CLP OH1 crystal. THz waves were generated over an extremely wideband range of 0.5 to 10 *THz*. Besides, the crystal thickness dependence of the THz-wave energy from the OH1 crystal was measured and the thicknesses of the OH1 crystals were 0.25, 0.40, 0.63, 0.85, and 1.05 *mm* respectively. The research proves the THz-wave output increased with increasing OH1 crystal thickness and the maximum output energy of the THz wave when the OH1 crystal of the thickness of 1.05 *mm* was used was 604 *pJ/pulse*.

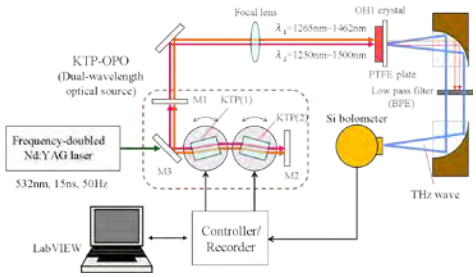

Fig. 1 Schematic diagram of the experimental setup for generating THz waves with an OH1 crystal by dual-wavelength KTP-OPO pumping.

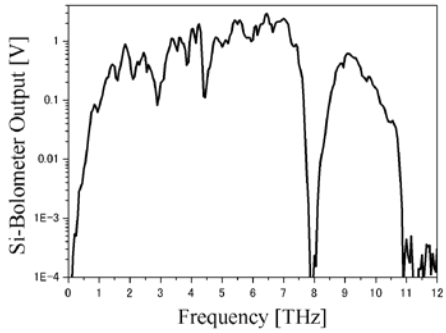

Fig. 2 THz wave spectra obtained by DFG using the OH1 crystal. The fundamental wavelength was fixed at λ_1 = 1265 *nm*. The resolution of the measured THz spectrum was 100 *GHz*. The THz frequency was tuned from 0.5 to 10 *THz* without a strong dip at approximately 1.1 *THz*.

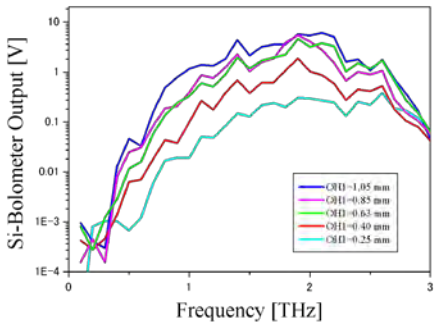

Fig. 3 Crystal thickness dependence of the THz-wave energy from the OH1 crystal. The fundamental wavelength was fixed at λ_1 = 1265 *nm*. The pump beam power density was 50 MW/cm^2. The THz-wave output increased with increasing OH1 crystal thickness, and the maximum output energy of the THz wave was 604 *pJ/pulse* when the THz frequency was 2.1 *THz*.

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