A comparative study of THz spectra

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Abstract: We have constructed two types of THz spectrometers using the frequency-tunable THz wave generators based on difference-frequency generation (DFG) in GaP crystal. The OPO-source system is for high accuracy measurement to detect fine structures in THz absorption spectra. The Cr:F-source system has merit in simple structure, easy maintenance and low-cost, but still has sufficient resolution for room temperature observation of solids or liquids. Comparing the absorption spectra of saccharides measured with these spectrometers and those measured with FT-IR or TDS, our spectrometers have superiority in frequency range and resolution, enough to record sub peaks, which can be analyzed as structural defects in organic compounds.

Key words: Terahertz; sweep-generator; spectrometer; GaP; LiNbO₃.

Introduction. In 1963, Nishizawa proposed generation of terahertz wave via the resonance of phonons as well as vibrations in molecule to fill the frequency gap between microwave and optical bands, 1), 2) just after the realization of semiconductor laser, which was also proposed by the same author in 1957 as the patent. 3) Loudon presented a similar proposal for THz wave generation by the use of a uniaxial crystal. 4) Yarborough et al. observed THz wave generation via dielectrics (LiNbO₃) 5) in 1969. Nishizawa and Suto developed a semiconductor GaP Raman laser in 1979. 6) In 1983 they generated a 12-THz wave with a peak power as high as 3 W, using a GaP Raman oscillator containing a GaAs mixing crystal. 7) In 1996, following the success on the GaP Raman laser by Nishizawa et al., Kawase et al. in the same institute reported an improvement of THz-wave generation efficiency by introducing a grating coupler on LiNbO₃. 8)

In 1998, when RIKEN started the second period in Photodynamics Research Center (PRC, which is Sendai branch of RIKEN), Nishizawa, as the director, planned to extend the experiment into dielectrics, and invited H. Ito to PRC for this task. In 2000, Kawase in Ito's group demonstrated a frequency-sweepable, high-power THz-wave generation using the parametric amplification effect of lattice vibrations, in the frequency range up to 2.5 THz, using LiNbO₃. 9), 10) Extremely high resolution spectral measurement of water and of HCl gas absorption was done with this method under Nishizawa's guidance. 11) In 2002, Tanabe, Suto and Nishizawa obtained more widely frequency-tunable, higher-power THz wave generation from GaP. The principle of this method is the difference frequency generation via resonance of phonon-polariton mode under small-angle noncollinear phase-matching conditions. 12)-14) Tunable frequency range was 0.3-7 THz and the maximum energy was 800 mW at 2.5 THz. In 2003, we constructed an automatic THz spectrometer using the GaP frequency-tunable THz wave generators and reported various spectra of biomolecules like saccharides, nucleoside, nucleotides, etc. 15)-17)

In this paper, we make a comparative study of THz absorption spectra measured with our system and those measured with other spectrometers, such as FT-IR (Fourier Transform InfraRed) spectroscopy, TDS (THz time domain spectroscopy). 18) As an example, transmittances of saccharides measured with different equipments are compared. Free electron laser 19) and p-Ge laser 20) can be also used as THz-wave sources for THz spectrometers. However, results obtained with these systems are not mentioned in this study, because these are special systems for experts.
Methods and materials. We have constructed two types of THz spectrometers using the frequency-tunable THz wave generators based on difference-frequency generation (DFG) in GaP crystal. Figure 1 shows a schematic diagram of the automatic measurement system for transmission spectroscopy.

The DFG of the first type (OPO-source system, Fig. 1 (a)) employs a Q-switched Nd:YAG laser with 10-Hz repetition rate and a $\beta$-BaB$_2$O$_4$ (BBO)-based Optical Parametric Oscillator (OPO) pumped by a 355 nm third harmonic beam of the YAG laser. Pulse width and linewidth were 11 ns and 0.003 cm$^{-1}$ for 1064 nm fundamental beam of the YAG laser, and 6 ns and less than 0.02 or 0.075 cm$^{-1}$ for the 1035-1064 nm tunable beam of the OPO laser, respectively. Absolute wavelength of OPO laser beam was calibrated by a double grating monochromator, of which absolute value was also calibrated by laser lines with 0.05 nm accuracy. Accuracy of generated THz-wavelength was also confirmed by observation of the water vapor absorption lines. The input powers of the both beams incident to the GaP crystal were reduced to 3 mJ by attenuators in order not to damage its surface. The pump and the signal beams were combined using a cubic polarizer placed on a rotating stage on a top of a linear stage, which automatically produced a very small angle between the two beams to fulfill the phase-matching condition and achieve a spatial overlap of the beam spots. The output direction of the THz wave depends on its frequency. This effect was compensated with a pair of off-axis parabolic reflectors, one of which was moving on a translation stage.

The spectrometer systems were built with the double beam method to obtain high S/N ratio. The THz-wave was divided into the sample and reference beams using a silicon beam splitter, which was wedge-shaped to prevent THz-wave resonance in the whole measurement range. Particularly for low temperature high resolution measurement, the sample beam was guided through a pellet mounted in the cryostat equipped with plastic windows, transparent for THz wave. Both, the sample and reference beams were measured with 4 K Si bolometers. Their detectivities were over 100 times higher than those of DTGS detectors, mentioned below.

The input ports of the bolometers were covered with black polyethylene films to cut-off near-IR light. The output signals of the bolometers were measured and processed by a digital oscilloscope. The whole measurement system was controlled with a personal computer (PC). Our own program controlled the wavelength of the beam, stage positions and data acquisition. The whole THz-wave path was purged with dry air to eliminate water vapor absorption.

In the second type THz wave generator (Cr:F-source system, Fig.1 (b)), we used two Cr:Forsterite (Cr:F) lasers for DFG. The Cr:F lasers were pumped by a Q-switched YAG laser with a 10 Hz repetition rate. The wavelength of the pump beam was fixed to 1210 nm. The linewidth was less than 0.01 nm with an etalon and 0.1 nm without an etalon. The wavelength of the signal beam was varied between 1210 and 1250 nm by tuning the prism dispersion and linewidth was below 0.1 nm. The pulsewidths and input powers of the both beams were 20-30 ns and 4 mJ, respectively. The other components of the THz spectrometers and their operation were almost the same. But pyroelectric deuterium triglycine sulfate (DTGS) detectors operated at room temperature were employed as THz-wave detector.

Tunable frequency range and power of THz-wave generated by the OPO-source and the Cr:F-source were almost the same in each other. The merits of the Cr:F-source system are simple structure, easy maintenance and low-cost. However, its spectral resolution is 30 GHz, while that for the OPO-source system is 1.5~3.2 GHz. Note that the resolution is sufficient for room temperature observation of solids or liquids.

On the other hand, the merit of the OPO system is high accuracy due to narrow linewidth of the THz-wave and high sensitive detectors. The decrease of S/N ratio for transmittance measurement is caused by fluctuation of the THz-wave power and noise of detector. Actually, the fluctuation of the THz-wave power, derived from both the source laser power fluctuation (~10%) and timing jitter fluctuation, was about 20% or more from pulse to pulse. However, the effect of the THz wave power fluctuation could be reduced by adopting the double beam method using the wedge-shaped Si beam splitter which enables to eliminate the THz-wave resonance completely. The fluctuation of transmittance was about 3% at around 3 THz by balancing the double beams.

The effect of the detector noise is dominant for decrease of S/N, if the THz-wave power is weak (below 1 THz or above 5 THz). However, by use of the low noise 4 K Si bolometer made possible to achieve high S/N ratio in wide frequency range. Both the cancellation of the fluctuation and noise reduction enables observation of fine structures presented in spectra. Finally, one of the noise sources at high power region is the mechanical vibration of the system.

The samples of crystalline saccharides consisted of
Fig. 1. Schematic diagram of THz spectrometer. OPO-source system (a) and Cr:F-source system (b).
D-(+)-glucose, D-(-)-fructose, D-(+)-galactose, D-(+)mannose and D-(+)-sucrose purchased from Tokyo Kasei Kogyo. Each sample was milled with polyethylene (PE) powder and pressed into 1-mm thick pellets (20 mm diameter) under a pressure of 2000 kg. Approximately 300 mg of PE was used for each sample. PE is a suitable filling material for THz (far-infrared) spectroscopy because it is very transparent. The concentrations of the saccharides were 5 or 10 wt%, chosen properly to exhibit clear absorption lines. The sample pellets were shaped into a wedge in order to prevent possible THz wave resonance via an etalon effect.

Results and discussion. Comparison of spectra by OPO-source system, by Cr:F-source system and by FT-IR at room temperature. Fig. 2 shows the transmittance spectra of glucose measured with the Cr:F-source system (black dots and line) in 15 GHz steps, with a linewidth better than 30 GHz (1 cm$^{-1}$), and with the OPO-source system (red dots and line) in 10 GHz steps, with a linewidth of 1.5 GHz (0.1 cm$^{-1}$), at room temperature, in the 0.5–6.0 THz (16.7–200 cm$^{-1}$) frequency region.

The transmittance spectra measured with the FT-IR, with 4 cm$^{-1}$ resolution and with 50 times averaging, are also shown in Fig. 2 (blue line). FT-IR spectra look very smooth, but this is the result of applied smoothing procedure. Note that the transmittance exceeding 100% below 2 THz is unreasonable. It must be owing to low S/N ratio due to low intensity of far-infrared light emitted by a mercury lamp. High resolution can be obtained with FT-IR, but the stroke of the Michelson interferometer must be extended as long as 6 m for the nominally highest resolution (0.001 cm$^{-1}$), which should be very sensitive to temperature fluctuation.

With the Cr:F-source system the spectra were possible to measure even below 0.8 THz with sufficient S/N ratio. General features of the main bands are almost the same as those obtained with FT-IR. But, fine structures, indicated by arrows in Fig. 2, could be observed.

With the OPO-source system the spectra were also possible to measure even below 0.8 THz and fine structures could be clearly observed. Distinctive features of signals are seen, for example, at 2.54, while such dips of transmittance are hardly observed with FT-IR.

In general, FT-IR is also a powerful tool even in the THz region, but mainly above 2 THz and only for dominant bands. In contrast, our system enables observation of not only dominant bands, but also of fine structures, even from below 0.8 THz, up to 5.7 THz. Superiority of our system is related to the THz source, which provides the THz wave with high energy density within a narrow frequency interval for every value of the tuned frequency.

Comparison of spectra by Cr:F-source system and by TDS at room temperature. The Cr:F-source system has the merit of a simple structure, easy maintenance and low-cost, whereas its spectral resolution is worse than that of the OPO-source system, as mentioned above. However, the resolution is sufficient for room temperature observation of solids or liquids. In this section, we are going to compare spectra measured with the Cr:F-source system and those with the TDS, which seems to have resolution of the same grade. A few papers have reported THz (far-infrared) spectra of saccharides measured with terahertz time-domain spectroscopy (TDS). Upadhya et al.$^{21}$ reported the temperature dependence of far-infrared vibrational modes of saccharides in the frequency range of 0.1-3.0 THz, using TDS. Walther et al.$^{22}$ reported absorption lines of the monosaccharides (glucose and fructose), and the disaccharide (sucrose), in the frequency range of 0.5-4.0 THz measured with TDS, and they also observed the temperature dependence of the spectra.

Figure 3 (a)-(e) shows molar absorption spectra of saccharides ((a)glucose, (b)fructose, (c)galactose, (d)mannose, (e)saccharose (sucrose)) measured with the Cr:F-source system at 294 K, in the 0.5–6.0 THz (16.7–200 cm$^{-1}$) frequency region, in 15 GHz steps, with a linewidth better than 30 GHz (1 cm$^{-1}$). The spectra were obtained with averaging of 32 pulses at each frequency.
These spectra can be compared with the spectra measured by TDS at 295 K, appeared in Ref. 21. These spectra were reproduced in Fig. 3 (a)-(d), but have offsets for clarity. For galactose (c), both the intensity and the frequency of absorption lines are almost the same up to 3 THz. However, for glucose (a), fructose (b) and mannose (d), the spectra by TDS show weaker peaks and dips than those by Cr:F-source system. This is remarkable in the 2-3 THz frequency region. For example, the absorption band at 2.7 THz in the fructose spectra, the full-width at half maximum (FWHM) of the band seems to be 230 GHz for the TDS and 160 GHz for the Cr:F-source system.

The absorption spectra measured by TDS at 300 K in Ref. 22 for glucose, fructose and for saccharose (sucrose) can also be compared with our results. These spectra were also reproduced in Fig. 3 (a), (b) and (e) with offsets for clarity. Scales of the absorption coefficients were inserted, because their absolute values of molar absorption cannot be converted. Absorption bands measured with TDS are almost the same as those with the Cr:F-source system up to 3 THz, but there seems a difference in the spectral width in 2.5-4 THz region. For example, the absorption band at 2.7 THz in the spectrum for fructose mentioned above, the FWHM of the band seems to be 260 GHz for TDS, while 160 GHz for Cr:F-source system. In the frequency range beyond 3 THz, the spectra by TDS seem to be considerably disturbed by noise. In the spectra for sucrose, the absorption band at 3.5 THz is apparently shifted to 3.3 THz.

TDS seems to be difficult in obtaining reliable spectra at frequencies exceeding 3 THz. Perhaps, the pulse width of the excitation laser is not short enough for the higher frequency generation. On the other hand, the Cr:F-source system can measure meaningful spectra up to 5.7 THz, which means that its frequency band width is nearly twice as wide as that for TDS. Extension of the THz frequency band should be beneficial for identifying molecules that differ slightly, such as conformational isomers. Actually, a lot of meaningful absorption lines could be observed outside of the frequency range of TDS.

Comparison of spectra by OPO-source system and by TDS at low temperature. OPO-source system can prove its merit of high resolution for materials which have sharp absorption bands, such as gases or solid samples at low temperature, in particular for observing fine structures of the spectra. Figure 4 shows molar absorption spectra of glucose measured at 20 K by the OPO-source system in the 0.5-6.0 THz (16.7-200 cm⁻¹) frequency region, in 10 GHz steps, with a linewidth of 1.5 GHz (0.05 cm⁻¹). The spectra were obtained with averaging of 32 pulses. Very sharp and well resolved absorption lines could be obtained due to high purity of generated THz wave and low noise measurement systems. Higher S/N ratio and wider frequency
range than for the Cr:F-source system results mainly from the high sensitivity of a 4 K-Si bolometer.

These spectra were compared with the spectra measured by TDS at 4 K appeared in Ref. 21 and at 10 K in Ref. 22. These spectra were reproduced in Fig. 4 with offsets. General features of the main bands measured by TDS are almost the same as those measured by OPO-source system up to around 3 THz. The FWHM of the absorption band at 1.45 THz is 30 GHz for OPO-source system, and 60 GHz for TDS. Residual noise level was evaluated to be 3% by measuring time change of Signal / Reference ratio at constant THz frequency around 3 THz. Peaks indicated by arrows in Fig. 4 must be the fine structures compared with noise level. The OPO-source system is superior in resolution and frequency range as compared with TDS.

In conclusion, we have constructed two types of THz spectrometers using the frequency-tunable THz wave generators based on difference-frequency generation (DFG) in GaP crystal. Comparison of the absorption spectra of saccharides measured with these spectrometers and the spectra measured with FT-IR or TDS proves that our spectrometers have wide bandwidth and high resolution.

Acknowledgement. This study was conducted as part of the Terahertz Optics Project for Medical Applications led by J. Nishizawa, organized by the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References


(Received Dec. 27, 2004; accepted Jan. 12, 2005)