IEICE TRANS. ELECTRON., VOL.E105–C, NO.2 FEBRUARY 2022

INVITED PAPER *Special Section on Electronic Displays*

Estimating the Birefringence and Absorption Losses of Hydrogen-bonded Liquid Crystals with Alkoxy Chains at 2.5 THz

Ryota ITO[†a)], **Hayato SEKIYA**[†], ***Nonmembers***, **Michinori HONMA**[†], ***and*** **Toshiaki NOSE**[†], ***Members***

SUMMARY Liquid crystal (LC) device has high tunability with low power consumption and it is important not only in visible region but also in terahertz region. In this study, birefringence and absorption losses of hydrogen-bonded LC was estimated at 2.5 THz. Our results indicate that introduction of alkoxy chain to hydrogen-bonded LC is effective to increase birefringence in terahertz region. These results indicate that hydrogen-bonded LCs are a strong candidate for future terahertz devices because of their excellent properties in the terahertz region.

key words: *terahertz, liquid crystal, hydrogen bonding, optically pumped gas laser*

1. Introduction

Terahertz waves have attracted significant attention for many years, owing to their promising applications including communication technologies, security checking, and nondestructive testing [1]. Recently, there have been extensive efforts to investigate terahertz wave control devices. Liquid crystals (LCs) are well known as excellent electro-optic materials and are strong candidates for high-performance terahertz wave control devices owing to their low power consumption and controllability at low drive voltages.

A material's properties in the terahertz frequency range must be fully understood before it can be used for terahertz applications. Researchers have thus aimed to clarify the optical properties of LCs in the terahertz region. For example, Nose et al. [2] reported that LCs exhibit birefringence in the terahertz frequency range by using an optically pumped far-infrared gas laser. Many others have since used terahertz time-domain spectroscopy systems to demonstrate the refractive indices of LCs in the terahertz range [3]–[15]. Based on these substantiated and attractive terahertz properties, LCs have attracted attention for usage in a variety of terahertz wave control devices. Pan et al. [16]–[19] developed a terahertz-tunable LC phase shifter, whereas Koch et al. [20] developed a tunable LC filter. Other reported LC-based tunable terahertz wave control devices have included a reflection-type phase shifter [21], an LC tunable metamaterial absorber [22], an LC phase grating device [23], and an LC-based vortex beam generator [24].

Since terahertz waves have longer wavelengths than their visible light counterparts, a thick LC layer is often needed for LC-based terahertz wave control devices. However, in general, the LC layer should be as thin as possible to allow fast operation and high birefringence LCs are effective to decrease the thickness of the LC layer. As such, LC materials exhibiting high birefringence in the terahertz range have been reported [25]–[27]. However, almost all previously reported LC materials exhibit dichroism in the terahertz range (i.e., the terahertz wave absorption varies depending on the polarization of the incident terahertz wave) [2]–[4], [8]–[13], [25]–[27]. This dichroism can cause unwanted variations in the intensity of the LC-based terahertz wave control devices. In our previous work, we confirmed that hydrogen-bonded LC with alkyl chain does not exhibit dichroism at 2.5 THz [28]. Nevertheless, the birefringence of this LC was not large as reported high-birefringence LCs [25]–[27].

In this study, we focus on hydrogen-bonded LC with alkoxy chains and estimate the birefringence and absorption losses at 2.5 THz. Here, the transmittance of the homogeneous alignment cell is measured using an optically pumped gas laser and birefringence and absorption losses of the hydrogen-bonded LC with alkoxy chains is estimated by using Jones matrix calculations.

2. Experimental

2.1 Measurement Methods

Figure 1 shows structure of a homogeneous alignment cell for terahertz measurements. To maintain a high transmittance of the terahertz wave, we used z-cut quartz substrates. The LC material 6380 (LCC, Japan) was injected into a sandwich cell. The 6380 contains the dimer of 4-alkoxybenzoic acid as shown in Fig. 2. Both of the inner surfaces of the substrates were treated with antiparallel rubbing after coating the planar alignment layer with polyimide (SE2170, Nissan Chemical Industries, Japan) to obtain homogeneous alignment. The cell thickness was determined by using sheet spacers. The LC layer was 800 μm thick.

Figure 3 shows the experiment setup. In this study, the terahertz wave intensity profiles were measured using an optically pumped gas laser as a terahertz source, as shown in the experimental setup that is summarized in Fig. 3. This laser is a coherent continuous wave source and delivers powerful terahertz radiation above 0.3 THz. A CO_2 laser was used to pump the CH_2F_2 gas, and a frequency of 2.5 THz was used for the measurements. The LC device was placed

---

Manuscript received March 15, 2021.
Manuscript publicized August 17, 2021.

[†] The authors are with Department of Intelligent Mechatronics, Akita Prefectural University, Yurihonjyo-shi, 015–0055 Japan.
a) E-mail: r_ito@akita-pu.ac.jp

DOI: 10.1587/transele.2021DII0003

between two wire-grid polarizers. To minimize the influence of laser power variation when measuring the intensity of the terahertz wave, two pyroelectric detectors were used. Thus, an accurate transmittance was obtained by normalizing the intensity of pyroelectric detector 2 by that of detector 1 (see Fig. 3).

2.2 Calculation Methods

The birefringence and absorption losses of the LC were evaluated by calculating the transmittance of the homogeneous cell using the Jones matrix method [28], [29]. Since the LCs have absorption loss in the terahertz region, we consider the influence of absorption loss in the Jones matrix calculation as follows [28]. Here, the electric field of the terahertz wave passing through the homogeneous cell can be written as

$$\begin{bmatrix} E_x \\ E_y \end{bmatrix} = \boldsymbol{P}_{\mathrm{A}}\boldsymbol{QWQ}\begin{bmatrix} \cos\Psi_{\mathrm{P}} \\ \sin\Psi_{\mathrm{P}} \end{bmatrix}, \tag{1}$$

where $\boldsymbol{P}_{\mathrm{A}}$, $\boldsymbol{Q}$, and $\boldsymbol{W}$ represent the Jones matrices of the analyzer, z-cut quartz substrate, and homogenous cell, respectively, and Ψ_{P} is the angle of the polarizer. Here, $\boldsymbol{P}_{\mathrm{A}}$ is calculated as

$$\boldsymbol{P}_{\mathrm{A}} = \boldsymbol{R}(\Psi_{\mathrm{A}})\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}\boldsymbol{R}(-\Psi_{\mathrm{A}}), \tag{2}$$

where Ψ_{A} is angle of the analyzer and $\boldsymbol{R}(\Psi)$ is the rotation matrix,

$$\boldsymbol{R}(\Psi) = \begin{bmatrix} \cos\Psi & -\sin\Psi \\ \sin\Psi & \cos\Psi \end{bmatrix}. \tag{3}$$

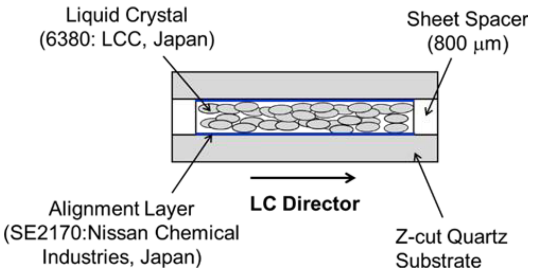


Fig. 1 Homogeneous alignment cell used in terahertz measurements.

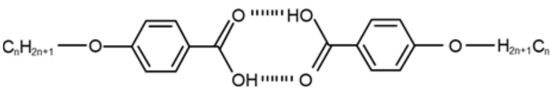


Fig. 2 Molecular structure of the hydrogen-bonded liquid crystal with alkoxy chains.

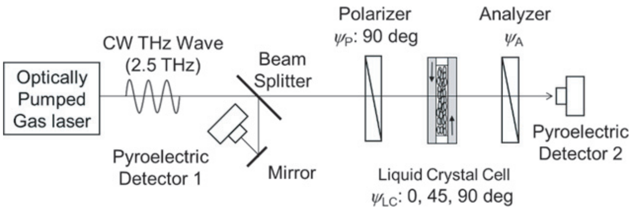


Fig. 3 Experimental setup.

Further, the Jones matrix of the z-cut quartz substrate (i.e., $\boldsymbol{Q}$), is written as

$$\boldsymbol{Q} = \exp\left(-\frac{2\pi n''_{\mathrm{q}} d_{\mathrm{q}}}{\lambda}\right)\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \tag{4}$$

where d_{q} and n''_{q} are the thickness and imaginary part of the refractive index of the z-cut quartz substrate, respectively, and λ is wave length of the terahertz wave.

The Jones matrix of the homogeneous cell ($\boldsymbol{W}$) is written as follow.

$$\boldsymbol{W} = \boldsymbol{R}(\Psi_{\mathrm{LC}})\begin{bmatrix} a & 0 \\ 0 & b \end{bmatrix}\boldsymbol{R}(-\Psi_{\mathrm{LC}}), \tag{5}$$

Here, a and b are written as

$$a = \exp\left(-\frac{i\Gamma}{2}\right)\exp\left(-\frac{2\pi n''_{\mathrm{e}} d_{\mathrm{LC}}}{\lambda}\right), \tag{6}$$

$$b = \exp\left(\frac{i\Gamma}{2}\right)\exp\left(-\frac{2\pi n''_{\mathrm{o}} d_{\mathrm{LC}}}{\lambda}\right), \tag{7}$$

where d_{LC} is the thickness of LC layer, n''_{e} and n''_{e} are the imaginary part of the extraordinary and ordinary refractive indices of the LC, respectively, and Γ can be calculated as

$$\Gamma = \frac{2\pi\Delta n d}{\lambda}, \tag{8}$$

where Δn is the birefringence of the LC.

3. Result and Discussion

Figure 4 shows the experimental and calculated terahertz transmittance values of the homogeneous cell using 6380 at 2.5 THz. The graph shows the transmittance as a function of analyzer angle Ψ_{A} when the direction of the polarizers $\Psi_{\mathrm{P}} = 90$ deg and the direction of LC director $\Psi_{\mathrm{LC}} = 0$, 45, and 90 deg as shown in Fig. 3. The measured and calculated data were in good agreement when $n''_{\mathrm{e}} = n''_{\mathrm{o}} = 0.028$ and $\Delta n = 0.19$. Here, $n''_{\mathrm{q}} = 0.0005$, corresponding with

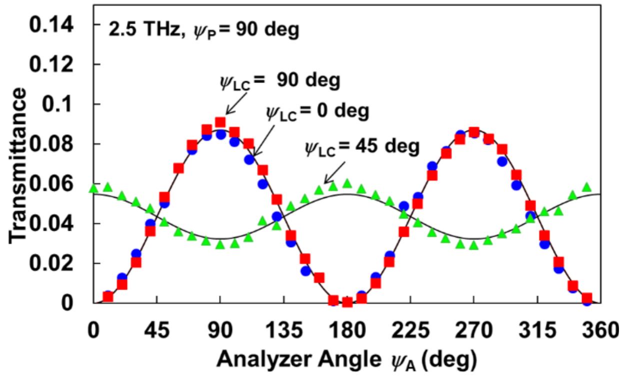


Fig. 4 Experimental and calculated terahertz transmittance of the homogeneous cell using LC 6380 at 2.5 THz, where the solid lines show the calculated results using the Jones matrix method.

$\alpha_q = 4\pi n''_q/\lambda = 0.5\ \text{cm}^{-1}$, and is consistent with previously reported values [30]. The tendency of $n''_e = n''_o$ is consistent with reported results of hydrogen-bonded LCs without alkoxy chains [28]. The estimated Δn of LC 6380 was 0.19, slightly greater than the reported value of 0.17 in a hydrogen-bonded LC without alkoxy chains [28]. The incensement of birefringence in the terahertz region by introducing alkoxy chain has been reported in LCs without hydrogen bonding [11]; the results presented here thus indicate that alkoxy chains can enhance birefringence in hydrogen-bonded LCs, as well. Further, the lower n''_e and n''_o value (i.e., 0.028 vs. 0.035 by [28]) is attractive for the development of future LC-based terahertz wave control devices. More-detailed measurements are in progress to characterize the broadband terahertz properties of hydrogen-bonded LCs.

4. Conclusions

The absorption losses and birefringence of a hydrogen-bonded LC at 2.5 THz were measured by using optically pumped gas laser. The experimental and calculated results indicate that the introduction of an alkoxy chain can increase the birefringence and ensure no dichroic absorption at 2.5 THz. Furthermore, the absorption loss of the hydrogen-bonded LC with alkoxy chains is lower than that of hydrogen-bonded LCs with alkyl chains. This work thus represents a significant step toward the development of LC-based terahertz wave control devices used in terahertz applications, which require no dichroism, low losses, and high birefringence.

Acknowledgments

This work was supported in part by JSPS KAKENHI Grant Number JP20K04625.

References

[1] M. Tonouchi, "Cutting-edge terahertz technology," Nat Photonics, vol.1, no.2, pp.97–105, Feb. 2007.

[2] T. Nose, S. Sato, K. Mizuno, J. Bae, and T. Nozokido, "Refractive index of nematic liquid crystals in the submillimeter wave region," Appl. Opt., AO, vol.36, no.25, pp.6383–6387, Sept. 1997.

[3] D. Turchinovich, P. Knobloch, G. Luessem, and M. Koch, "THz time-domain spectroscopy on 4-(trans-4'-pentylcyclohexyl)-benzonitril," Liq Cryst V, vol.4463, pp.65–70, Dec. 2001.

[4] T.-R. Tsai, C.-Y. Chen, C.-L. Pan, R.-P. Pan, and X.-C. Zhang, "Terahertz time-domain spectroscopy studies of the optical constants of the nematic liquid crystal 5CB," Appl. Opt., AO, vol.42, no.13, pp.2372–2376, May 2003.

[5] Y. Takanishi, K. Ishikawa, J. Watanabe, H. Takezoe, M. Yamashita, and K. Kawase, "Terahertz spectroscopy in smectic phases of a bent-core molecule," Phys. Rev. E, vol.71, no.6, p.061701, June 2005.

[6] J. Nishizawa, T. Yamada, T. Sasaki, T. Tanabe, T. Wadayama, T. Tanno, and K. Suto, "Terahertz dichroism of MBBA liquid crystal on rubbed substrate," Appl Surf Sci, vol.252, no.12, pp.4226–4229, April 2006.

[7] S. Tanaka, Y. Okada, K. Yamamoto, Y. Takanishi, M. Tani, K. Ishikawa, M. Hangyo, and H. Takezoe, "Effect of permanent dipole moments perpendicular to the molecular long axis on the terahertz absorption in liquid crystals," Emerg Liq Cryst Technol II, vol.6487, p.648708, Feb. 2007.

[8] R.-P. Pan, C.-F. Hsieh, C.-L. Pan, and C.-Y. Chen, "Temperature-dependent optical constants and birefringence of nematic liquid crystal 5CB in the terahertz frequency range," J Appl Phys, vol.103, no.9, p.093523, May 2008.

[9] R. Wilk, N. Vieweg, O. Kopschinski, T. Hasek, and M. Koch, "THz Spectroscopy of Liquid Crystals from the CB Family," J Infrared Milli Terahz Waves, vol.30, no.11, pp.1139–1147, Nov. 2009.

[10] O. Trushkevych, H. Xu, T. Lu, J.A. Zeitler, R. Rungsawang, F. Gölden, N. Collings, and W.A. Crossland, "Broad spectrum measurement of the birefringence of an isothiocyanate based liquid crystal," Appl. Opt., AO, vol.49, no.28, pp.5212–5216, Oct. 2010.

[11] N. Vieweg, M.K. Shakfa, B. Scherger, M. Mikulics, and M. Koch, "THz Properties of Nematic Liquid Crystals," J Infrared Milli Terahz Waves, vol.31, no.11, pp.1312–1320, Nov. 2010.

[12] C.-S. Yang, C.-J. Lin, R.-P. Pan, C.T. Que, K. Yamamoto, M. Tani, and C.-L. Pan, "The complex refractive indices of the liquid crystal mixture E7 in the terahertz frequency range," J. Opt. Soc. Am. B, JOSAB, vol.27, no.9, pp.1866–1873, Sept. 2010.

[13] N. Vieweg and M. Koch, "Terahertz properties of liquid crystals with negative dielectric anisotropy," Appl. Opt., AO, vol.49, no.30, pp.5764–5767, Oct. 2010.

[14] N. Vieweg, B.M. Fischer, M. Reuter, P. Kula, R. Dabrowski, M.A. Celik, G. Frenking, M. Koch, and P.U. Jepsen, "Ultrabroadband terahertz spectroscopy of a liquid crystal," Opt. Express, vol.20, no.27, pp.28249–28256, Dec. 2012.

[15] M. Reuter, K. Garbat, N. Vieweg, B.M. Fischer, R. Dąbrowski, M. Koch, J. Dziaduszek, and S. Urban, "Terahertz and optical properties of nematic mixtures composed of liquid crystal isothiocyanates, fluorides and cyanides," J Mater Chem C, vol.1, no.29, pp.4457–4463, July 2013.

[16] C.-Y. Chen, T.-R. Tsai, C.-L. Pan, and R.-P. Pan, "Room temperature terahertz phase shifter based on magnetically controlled birefringence in liquid crystals," Appl. Phys. Lett., vol.83, no.22, pp.4497–4499, Nov. 2003.

[17] C.-F. Hsieh, R.-P. Pan, T.-T. Tang, H.-L. Chen, and C.-L. Pan, "Voltage-controlled liquid-crystal terahertz phase shifter and quarter-wave plate," Opt. Lett., OL, vol.31, no.8, pp.1112–1114, April 2006.

[18] C.-Y. Chen, C.-L. Pan, C.-F. Hsieh, Y.-F. Lin, and R.-P. Pan, "Liquid-crystal-based terahertz tunable Lyot filter," Appl. Phys. Lett., vol.88, no.10, p.101107, March 2006.

[19] I.-C. Ho, C.-L. Pan, C.-F. Hsieh, and R.-P. Pan, "Liquid-crystal-based terahertz tunable Solc filter," Opt. Lett., OL, vol.33, no.13, pp.1401–1403, July 2008.

[20] N. Vieweg, N. Born, I. Al-Naib, and M. Koch, "Electrically Tunable Terahertz Notch Filters," J Infrared Milli Terahz Waves, vol.33, no.3, pp.327–332, March 2012.

[21] L. Wang, S. Ge, W. Hu, M. Nakajima, and Y. Lu, "Tunable reflective liquid crystal terahertz waveplates," Opt. Mater. Express, OME, vol.7, no.6, pp.2023–2029, June 2017.

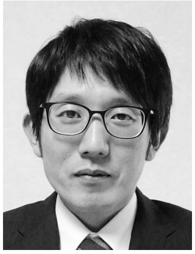
[22] D. Shrekenhamer, W.-C. Chen, and W.J. Padilla, "Liquid crystal tunable metamaterial absorber," Phys. Rev. Lett., vol.110, no.17, p.177403, April 2013.

[23] C.-J. Lin, Y.-T. Li, C.-F. Hsieh, R.-P. Pan, and C.-L. Pan, "Manipulating terahertz wave by a magnetically tunable liquid crystal phase grating," Opt. Express, OE, vol.16, no.5, pp.2995–3001, March 2008.

[24] S. Ge, P. Chen, Z. Shen, W. Sun, X. Wang, W. Hu, Y. Zhang, and Y. Lu, "Terahertz vortex beam generator based on a photopatterned large birefringence liquid crystal," Opt. Express, vol.25, no.11, pp.12349–12356, May 2017.

[25] N. Vieweg, M.K. Shakfa, and M. Koch, "BL037: A nematic mixture with high terahertz birefringence," Opt Commun, vol.284, no.7,

pp.1887–1889, April 2011.
[26] L. Wang, X. Lin, X. Liang, J. Wu, W. Hu, Z. Zheng, B. Jin, Y. Qin, and Y. Lu, "Large birefringence liquid crystal material in terahertz range," Opt. Mater. Express, vol.2, no.10, pp.1314–1319, Oct. 2012.
[27] M. Reuter, N. Vieweg, B.M. Fischer, M. Mikulicz, M. Koch, K. Garbat, and R. Dąbrowski, "Highly birefringent, low-loss liquid crystals for terahertz applications," APL Mater, vol.1, no.1, p.012107, June 2013.
[28] R. Ito, M. Honma, and T. Nose, "Electrically tunable hydrogen-bonded liquid crystal phase control device," Appl Sci, vol.8, no.12, p.2478, Dec. 2018.
[29] R.C. Jones, "A new calculus for the treatment of optical systems I. Description and discussion of the calculus," J Opt Soc Am., vol.31, no.7, pp.488–493, July 1941.
[30] D. Grischkowsky, S. Keiding, M. van Exter, and C. Fattinger, "Far-infrared time-domain spectroscopy with terahertz beams of dielectrics and semiconductors," J. Opt. Soc. Am. B, vol.7, no.10, pp.2006–2015, Oct. 1990.



Ryota Ito was born in 1981. He received B.S degrees of engineering form Akita Prefectural University in 2004. He received M.S. degree in electronic engineering from Tohoku University in 2006. From 2006 to 2012, he was a research associate at Akita Prefectural University. He then obtained his Ph.D. degree in electronics engineering from Osaka University in 2012. Since 2012, he has been an assistant professor at Akita Prefectural University, where he has been engaged in research on THz waves and liquid crystal devices.

Hayato Sekiya was born in 1996, and received his B.S. from Akita Prefectural University. His main research interest is on the liquid crystal devices for terahertz frequency region.

Michinori Honma was born in 1972. He received master's and doctoral degrees of engineering form Akita University in 1997 and 2000, respectively. Since 2000, he has been engaged in the research on liquid crystal optical devices in Akita Prefectural University. From April 2000 to September 2004, he was a research associate, and from October 2004, he has been an associate professor. He is a member of the Optical Society, the Japan Society of Applied Physics, the Optical Society of Japan, and the Japanese Liquid Crystal Society.

Toshiaki Nose received his B.S. degree in electrical engineering and his M.S. degree in electronic engineering from Tohoku University, Sendai, Japan, in 1983 and 1985, respectively. Since 1985 he had been a Research Associate at Akita University, Akita, Japan and he received ph.D. degree in electronics engineering from Tohoku University in 1995. Since 1999 he has been Professor at Akita Prefectural University, Yurihonjyo, Japan. He has been engaged on research works for liquid crystal optical device applications, and recently it is extended to millimeter-waves and THz waves.