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Xuemei Zheng, Colin V. McLaughlin, P. Cunningham, L. Michael Hayden,
"Terahertz science and applications based on poled electro-optic polymers,"
Proc. SPIE 6472, Terahertz and Gigahertz Electronics and Photonics VI,
64720F (1 February 2007); doi: 10.1117/12.696650

SPIE.

Event: Integrated Optoelectronic Devices 2007, 2007, San Jose, California,
United States

Terahertz science and applications based on poled electro-optic polymers

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ABSTRACT

We review recent research using amorphous electrooptic (EO) polymers for generation and detection of broadband terahertz radiation (0.3 THz -30 THz). The advantages of amorphous EO polymers over other materials for broadband THz generation (via optical rectification) and detection (via EO sampling) include a lack of phonon absorption (good transparency) in the THz regime, high EO coefficient and good phase-matching properties, and, of course, easy fabrication (low cost). Our ~12-THz, spectral gap-free THz system based on a polymer emitter-sensor pair is an excellent demonstration of the advantages of the use of EO polymers. This system has been employed as a wideband spectrometer to study dielectric materials in the THz regime.

Keywords: electrooptic polymer, nonlinear optics, optical rectification, terahertz, spectroscopy

1. INTRODUCTION

Terahertz (THz) radiation, with a loose definition between 0.3 THz and 30 THz ($1\text{THz} = 10^{12}\text{ Hz}$), bridges microwave and infrared (IR) radiation. A variety of excitations, such as rotational and vibrational states in molecular systems, lattice resonance in dielectric crystalline materials, and confinement states in artificially fabricated nano-structures, occur in this spectral regime, suggesting its versatile applications in chemical and biological detection, medical imaging, and spectroscopy. For this reason, generation and detection of pulsed (equivalently, broadband) THz radiation using ultrashort lasers has been under intensive investigation in the past two decades. The greatest advantage of using broadband THz radiation for spectroscopic study is that an overall snapshot of the spectral characteristics of a sample in the THz regime can be obtained.¹ To achieve its most potential in scientific and technological arenas, a wide THz bandwidth with a smooth frequency response using low power laser sources would be very valuable.

Currently, optoelectronic and all-optical techniques are commonly employed for generation and detection of pulsed THz radiation. The optoelectronic technique relies on the use of photoconductive dipole antennas (PDA) fabricated as microstriplines or coplanar transmission lines on photoconductive inorganic substrates.^{2,3} These PDAs have excellent sensitivity and a smooth frequency response but a narrow useable bandwidth. The all-optical technique uses optical rectification (OR)⁴ in electro-optic (EO) materials to generate and uses EO sampling^{5,6} to detect the THz radiation. This method has good sensitivity and a large bandwidth, but the conventional systems consisting of crystalline EO materials do not have a smooth frequency response across that bandwidth due in part to phonon absorption associated with the crystalline nature of the emitters and detectors.

Since the first reports on generation and detection of THz radiation using poled EO polymers,^{6,7} organic EO polymer family have become an alternate to crystalline EO materials and recent THz systems based on EO polymers have shown greater emission efficiency^{8,9} and broader bandwidth free of spectral gaps^{10,11} compared with their crystalline counterparts. With better EO polymers being developed continuously, it can be envisioned that EO polymers will take a larger role in the near future.

In this paper, we will review our work on the generation and detection of the THz radiation using EO polymers in the past a few years. We will go over the fabrication of high-quality EO polymer films and how to use them to generate and detect the THz radiation. Some important results from our experiments and simulations are shown in the paper, too.

2. EO POLYMERS

2.1 Basics of EO polymers

A typical EO polymer consists of an active component — nonlinear optical (NLO) chromophores, and a passive component — a polymer matrix. Generally, a typical NLO chromophore is characterized by a π -electron conjugated bridge terminated by an electron-rich donor group (usually an amine and often grouped with an aromatic ring, such as an aniline derivative) on one end and an electron-deficient group (usually containing hetero atoms in high oxidation states and sometimes grouped with additional alkene content) on the other end.¹² High dipole moment (μ) and molecular hyperpolarizability (β) are the keys for design and synthesis of NLO chromophores with large nonlinearity. Advancement of EO polymers mostly depends on advancement of NLO chromophores. Intensive work by material engineers has results in quite some novel NLO chromophores that can lead to EO polymers with extremely high EO coefficients¹³⁻¹⁵ if appropriately used.

Selection of the passive polymer matrix is also very important in order to make high quality films with good stability. Generally, sufficient high glass transition temperature (T_g), capability of processing into films, and physical compatibility with NLO chromophores (allowing a sufficient amount of chromophores to be incorporated into the polymer) should be taken into consideration, as well as good transparency in both the optical and THz regime.¹² It is essential that the intrinsic T_g of the selected polymer is high, as the inclusion of the chromophore molecules into the polymer matrix reduces T_g . The resultant T_g of the EO polymer system should fall into a useful range for poling and stability.

After the film making, electric field poling is performed to orient the NLO chromophore molecules so as to break the centrosymmetric structure of the material and allow for bulk EO coefficients. Poling temperature is usually set at or just below T_g such that the chromophore molecules are mobile and can easily be oriented.¹² A too high T_g not only causes difficulty for operation, but might also exceed the thermo-chemical stability of the chromophore. On the other hand, a too low T_g can cause a rapid loss of the poling order at the device operation temperature, usually room temperature.

2.2 Freestanding EO polymer films for THz applications

Among the many options available as the polymer hosts and the NLO chromophores and with widely available Ti: sapphire lasers intended to be used for the THz generation and detection, we found that EO polymers consisting of amorphous polycarbonate (APC) copolymer as the host and Lemke dye [see Fig. 1(a)] or DCDHF-type dye [see Fig. 1(b)] as the guest worked the best. APC is commercially available and likely to form high optical-quality films, with an intrinsic T_g at 205° (sufficiently high to permit the addition of an adequate guest chromophores). To make easy references, we name the EO polymer based on Lemke as LAPC and that based on DCDHF as DAPC.

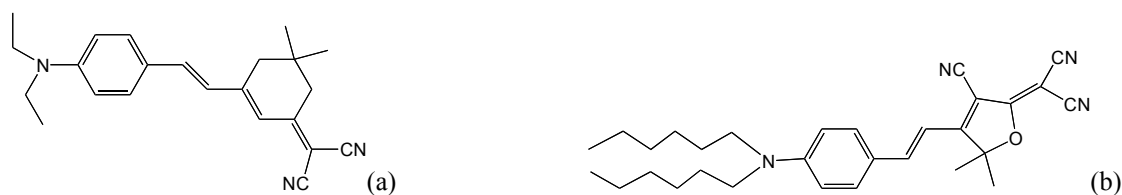


Figure 1. Chemical structure of the dye molecules, (a) Lemke and (b) DCDHF-6-V.

To make LAPC (40% Lemke/60% APC) and DAPC (40% DCDHF/60% APC) films,^{8, 12, 16} the first step is dissolving each component in dichloroethane in a 10% solids/solvent ratio. The films are then cast from the solution onto glass substrates coated with indium tin oxide (ITO). After solvent evaporation, two solid polymer films are pressed in vacuum 70 °C above its glass transition temperature T_g for 10 ~ 15 minutes. The thickness of the resulting film is controlled by appropriate polyimide spacers. High-optical-quality films with thickness in the range of 50-350 μm can be obtained with this method. After the film making, sufficient electric poling is performed so as to achieve high EO coefficients. A poling field as high as ~100 V/ μm can routinely be applied without causing breakdown in the polymers. At this level of poling, $r_{33} > 50 \text{ pm/V}$ and $r_{33} > 30 \text{ pm/V}$ at 785 nm can be achieved. The EO coefficients are measured with the

ellipsometric method.¹⁷ Because a THz wave does not transmit the conductive ITO coatings very well, it is important to remove at least one substrate with the ITO coating such that the ITO coating won't interact with the THz wave. In the case that laser pulses are very short (<50 fs FWHM), the other substrate should also be removed in order not to broaden the laser pulse duration.

3. TERAHERTZ SYSTEMS BASED ON EO MATERIALS

3.1 Optical rectification

Pioneering work using optical rectification in EO materials to generate electromagnetic radiation was first done by Shen *et al.*⁴ The crucial point for the development of this technique arrived when Auston *et al.* extended this technique by using shorter laser pulses and observed generated electromagnetic wave in the THz regime.¹⁸ Since then, many researchers have followed and further developed this technique by exploiting numerous materials and geometries.^{7, 19-22}

Optical rectification can be understood as mixing of two different frequency components in the frequency spectrum of an incident ultrashort optical pulse in an EO medium. As in every nonlinear wave mixing process, phase-matching condition determines the optimal interaction length and conversion efficiency of OR.²³ The OR process involves two optical photons (with the energy difference being the THz photon energy) and one THz photon, so the phase-matching condition is: $\Delta k = k_{opt}(\omega - \Omega) - k_{opt}(\omega) + k_{THz}(\Omega) = \Omega[n_g(\omega) - n_{THz}(\Omega)]/c = 0$. In the case of phase-mismatching ($\Delta k \neq 0$), coherence length (optical interaction length) can be expressed as: $l_c = \pi / \Delta k = \pi c / [\Omega(n_g - n_{THz})]$.²³ Clearly, a better phase-matching leads to a longer coherence length and potentially greater THz generation. Inorganic ZnTe crystal has been a standard material for the generation of the THz radiation, as there exists a good phase-matching for 800-nm-wavelength (readily available from commercial Ti: sapphire lasers) pump and ~2-THz radiation.

One problem for using crystalline materials, like ZnTe, is phonon absorption in the THz regime [the transverse optical (TO) phonon resonance of ZnTe occurs at ~5.3 THz²⁴]. In addition, a large dispersion of the THz index exists near any absorption band. This can have a significant influence on the phase matching. We still take ZnTe as the example. Its wide employment in the THz generation (and detection) is mostly due to the fact that there exists a good phase-matching at ~2 THz for the optical pump wavelength of ~800 nm (the emission wavelength of widely available femtosecond Ti: sapphire lasers). However, the dispersive nature of THz index²⁵ makes the good phase-matching region very narrow. For this reason, in order to achieve broadband THz emission, a very thin ZnTe crystal is essential, making the conversion efficiency low, not to mention the high cost of the crystal preparation. As will be discussed in the section 3, organic EO polymers do not have lattice structures and consequently do not have phonon absorption and serious THz index dispersion problems, suggesting their promising role as broadband THz emitters.

3.2 EO sampling

Free-space EO sampling is one of the standard techniques for coherent detection of THz radiation (the other is photoconductive sampling). It was first demonstrated for the THz detection by Wu *et al.*⁵ This technique involves the use of an EO material whose birefringence is transiently modified by a THz pulse field. The THz field induced birefringence change leads to a change of the polarization state of a probe beam that goes through the material at the moment. For good measurement sensitivity, a high EO coefficient is desired from the EO material, and for an undistorted measurement, the material should have both a good phase-matching property and good transparency across a bandwidth as broad as possible. Unfortunately, as mentioned above, crystalline EO materials all have phonon absorptions and accordingly dispersive refractive index in the THz regime, due to their intrinsic lattice resonance. The former one results in spectral gaps (distortion) for measured signals, and the latter one results in walk-off effect (distortion again) and limits the interaction length.

3.3 General set-up

A typical THz system based on EO materials is shown in Fig. 2. An output laser beam from a femtosecond laser is split into two beams, with the most power going to the pump beam to induce OR in a piece of EO material (THz emitter) and very little power going to the probe beam that interacts with the THz wave under investigation in another piece of EO material (THz sensor). By varying the optical delay line in one arm, the probe pulse (with duration much shorter than the

THz pulse) sees different parts of the THz waveform. The compensator is used to optically bias the phase retardation at the $\pi/2$ such that the EO detection works in the most linear regime. The differential detection scheme minimizes the influence of laser noise. With the delay line position and data acquisition controlled by a computer, we can map out the electric field (instead of power) of the THz wave. This gated sampling technique allows for jitter-free phase coherent detection, leading to a high signal-to-noise ratio (SNR) and dynamic range.

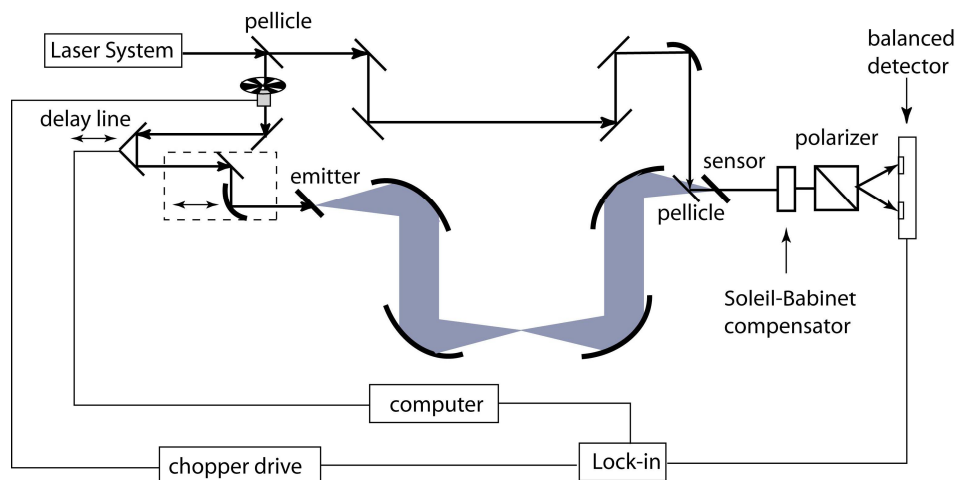


Figure 2. Schematic of the experimental set-up.

4. EXPERIMENTS

4.1 Efficient THz emitters based on EO polymers

It is expected that EO polymers are more efficient THz emitters than ZnTe, as the former has EO coefficients at least one order of magnitude higher than the latter. Considering the transverse poling geometry (poling field normal to the surface) and the p -polarization of the pump beam in our experiments, we need to orient the polymer film such that the pump beam is incident at Brewster's angle in order to achieve the maximal THz emission. Because of this geometry, roughly half of the magnitude of the nonlinearity of the EO polymers can be accessed. Even so, in our experiments with a 50-fs-duration, 800-nm-wavelength, 1-kHz, Ti: sapphire laser amplifying system (SpectraPhysics Spitfire) we found that an 80 μm thick EO polymer film generates more THz emission (per optical pump photon) than a 1000- μm -thick ZnTe crystal (see Fig. 3).

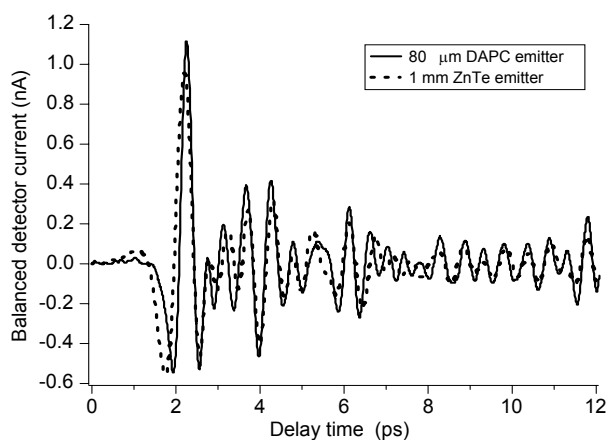


Figure 3. Comparison of the THz field emitted from a 1 mm ZnTe crystal and an 80 μm polymer layer (40%DCDHF-6-V/60%APC). The EO coefficient of the polymer is 47 ± 2 pm/V, in comparison to ~ 4 pm/V for ZnTe. The detection was done by using EO sampling with a 2 mm ZnTe.

4.2 Spectral gap-free THz radiation from a polymer emitter-sensor pair

As pointed out above, one advantage of using EO polymers for the THz generation and detection is the absence of phonon absorption. Our experiment indeed demonstrated it.¹⁰ Figure 4 shows the smooth spectrum up to ~12 THz from an LAPC emitter-sensor pair. Also shown in Fig. 4, is the THz spectrum emitted from the same LAPC emitter and measured by an 80- μm -thick ZnCdTe sensor. A wide spectral gap at ~5 THz can clearly be identified, which corresponds to the TO phonon absorption of the ZnCdTe crystal. If crystalline EO materials are used for a THz spectroscopic system, information within the spectral gaps cannot be extracted. On the contrary, polymer-based THz systems do not suffer from this limitation.

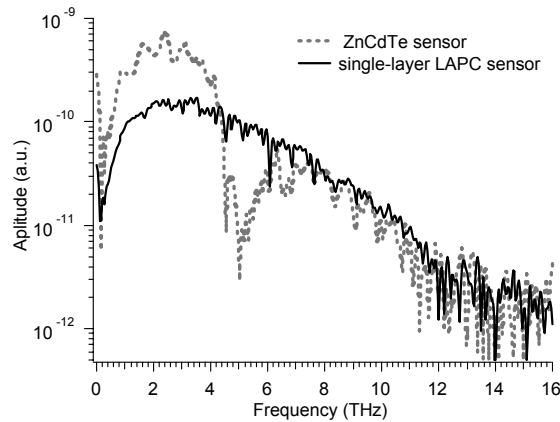


Figure 4. Comparison of the THz spectra with an 80- μm ZnCdTe sensor and a single-layer LAPC sensor. The same single-layer LAPC emitter is used in the two cases. The wide spectral gap in the case of ZnCdTe sensor is due to the phonon absorption associated with the lattice resonance of the crystal.

4.3 Phase-mismatch issue

Using the ~12-THz-bandwidth system based on the LAPC emitter-sensor pair, we studied dielectric properties of a variety of materials following the recently developed technique of THz time-domain spectroscopy (THz-TDS).²⁶ One important study we conducted was the measurement of the THz index of LAPC. The result from this study helped us evaluate the phase-matching capability of the material. As expected, the THz index of LAPC is approximately constant, as shown in Fig. 5. Comparing this with the previously obtained group index of LAPC, we found out that at ~800 nm there does not exist good phase matching for LAPC [$n_g(800\text{ nm}) \neq n_{\text{THz}}$]. The good phase-matching point occurs for the optical wavelength of ~1300 nm.

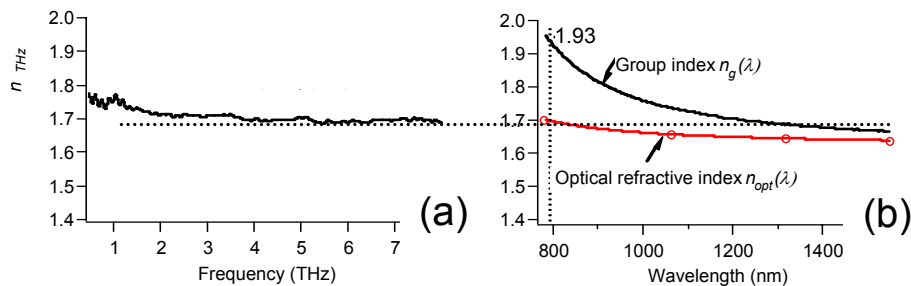


Figure 5. (a) Refractive indices of LAPC in the THz regime, measured using THz-TDS. (b) Derived refractive indices and group indices of LAPC in the optical regime. Open circles are measured refractive indices of LAPC at 780 nm, 1064 nm, 1319 nm, and 1550 nm, respectively.

The phase-matching condition determines the optimal interaction length (the coherence length) for both THz emitters and sensors based on EO materials. Because the coherence length is dependent on frequency, phase-mismatch induced spectral dips are expected for either a thick emitter or a thick sensor or their combination. Our experiments clearly demonstrate this. Four layers of freestanding LAPC films with thickness controlled by $\sim 75\text{-}\mu\text{m}$ -thick spacers, and one layer of LAPC with a thickness controlled by a $\sim 120\text{-}\mu\text{m}$ -thick spacer, were prepared using the method described above. The thick film was used as the THz sensor, while the other four were used as the THz emitter. By stacking the films up one by one, each oriented with the same poling polarity, we obtained multi-layer emitters. The employment of the multi-layer emitters is due to the fact that it is difficult to pole $>100\text{-}\mu\text{m}$ thick polymer films with a voltage high enough to obtain good EO coefficients in our lab.

Figure 6 shows the amplitude spectra of the THz fields from the four stacked LAPC emitters, using the same LAPC sensor in each case. The $\sim 12\text{-THz}$ bandwidth free of any spectral gap from the single-layer emitter-sensor pair has been shown as above (see Fig. 5). For the two-layer LAPC emitter, the observable bandwidth is narrowed to $\sim 11\text{ THz}$. It is very interesting to note that, for the three- and four-layer thick LAPC emitter, there are clear phase-mismatch induced spectral dips. For the former one, the dip is located around 5 THz , and for the latter one, one dip is located at $\sim 4\text{ THz}$ and the other at $\sim 8\text{ THz}$. Our modeling work, using the measured optical group index, THz index, and laser-related pulse parameters, shows that these dips match our prediction.¹¹

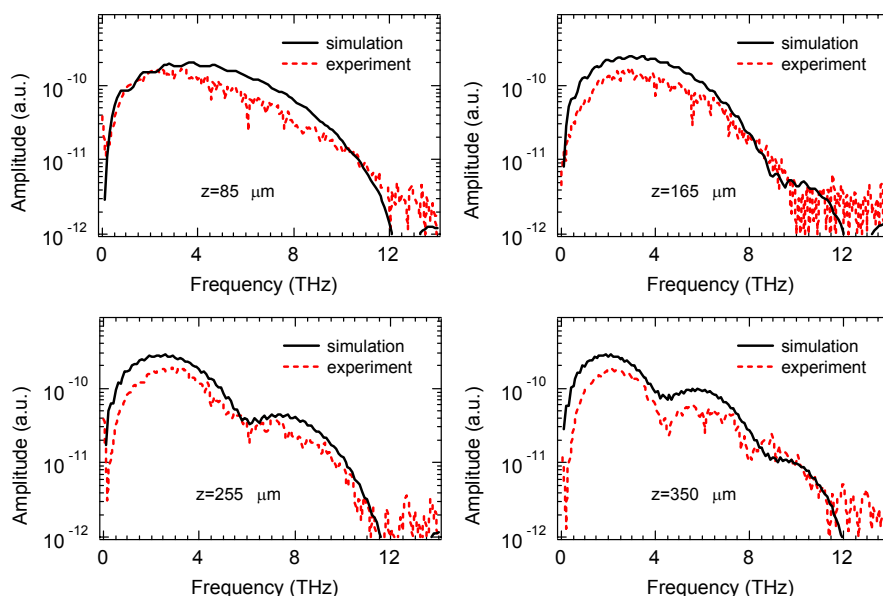


Figure 6. Comparison of the simulation work (solid lines) with experimental results (dashed lines) for multi-layer LAPC emitters.

4.4 Polymer emitter/sensor operate at telecommunication wavelength

For field THz applications, portable systems are highly desired. As light sources are usually the most bulky part of THz systems, reduction of the size of the light sources is crucial. In this sense, femtosecond fiber lasers (usually emitting at $>1\text{-}\mu\text{m}$ wavelength) are the most promising candidates. So far, very few materials are suitable for the THz generation and detection using the emission wavelengths of fiber lasers. Thanks to more than twenty years of intensive study driven by the telecommunication industry crying for cheap EO devices and easy integration, EO polymers with both high EO coefficients and high glass transition temperature (good thermal stability) are available now.¹³⁻¹⁵ With certain material modification, THz technology can also benefit from this advancement.

At this point, DAPC and LAPC are two mature EO composites ready for THz application. Measurements of their refractive indices in both the optical and THz regime show that in the wavelength tuning range (1260 nm – 1500 nm) of typical optical parametric amplifiers (OPA), both materials have better phase-matching. The shortcoming for the two materials, however, is that their EO coefficients in the OPA tuning range are not very high: $r_{33} < 20$ pm/V. Nevertheless, we have used these two materials in THz systems with very low pump power (<7 mW).

In one experiment, we tuned the OPA to ~1300 nm, used a ~75- μ m-thick DAPC as the THz emitter, and either a 2-mm-thick ZnTe or a 80- μ m-thick ZnCdTe as the THz sensor. The measured time-domain THz waveforms and corresponding frequency-domain THz spectra are shown in Fig. 7. In both cases, < 7 mW (measured after the mechanical chopper) optical pump power illuminated the emitter. In addition to the clear demonstration of the capability of EO polymers of generating THz radiation with ~1300-nm-wavelength pump, we also observe the significant phase-mismatching induced effect due to the use of ZnTe. It is known that ZnTe and ZnCdTe have very similar dielectric properties and EO coefficients. However, we observed that the much thicker ZnTe did not provide much larger THz signal than the ZnCdTe. This can only be explained by the significant phase-mismatching and/or THz absorption condition in the ZnTe. In Fig. 7, the spectrum associated with the ZnTe clearly shows many phase-mismatching induced spectral dips. It should be noted that the oscillations on the top of the spectrum corresponding to the thin ZnCdTe sensor is due to the multiple reflections in the crystal, confirmed by the oscillation period and the crystal thickness. Our modeling work can exactly predict the results shown here (see Fig. 7). This experiment is a good example to show the importance of the good phase-matching in the THz generation and detection system. In a recent study on the phase-matching in OR, van der Valk *et al.*²⁷ also observed spectral dips from ZnTe emitters using an optical parametric oscillator and successfully modeled these dips.

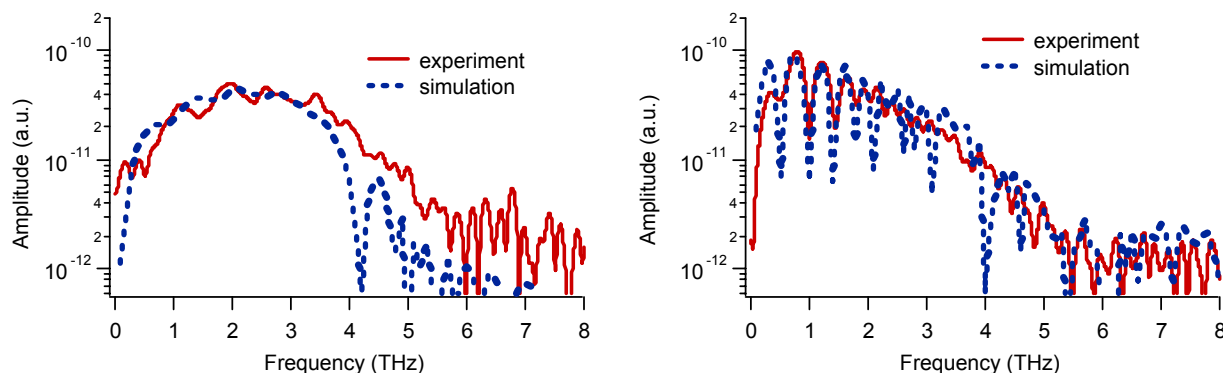


Figure 7. Comparison of the modeling work with the experimental results for the DAPC emitter-ZnCdTe/ZnTe sensor pairs, operated at ~1300 nm.

Because of the existing phonon absorption at ~5.3 THz in ZnCdTe, even for the 80- μ m-thick ZnCdTe, we could not observe bandwidth broader than 5 THz. We wanted to check the bandwidth performance of the EO polymers. Therefore, we used a 60- μ m-thick *c*-cut DAST as the THz emitter, since DAST has quite high EO coefficients at the wavelength and the THz absorption due to its multiple phonon bands is expected to be small (because of the weak intermolecular interaction) in the thin DAST. LAPC was used as the THz sensor in this case. The experimental results are shown in Fig. 8. Clearly, >10-THz bandwidth is possible to achieve with this emitter-sensor combination. Because of the smooth and broadband response of the EO polymers, we can confidently conclude that the spectral dips seen on the spectrum are actually due to the DAST lattice resonances.

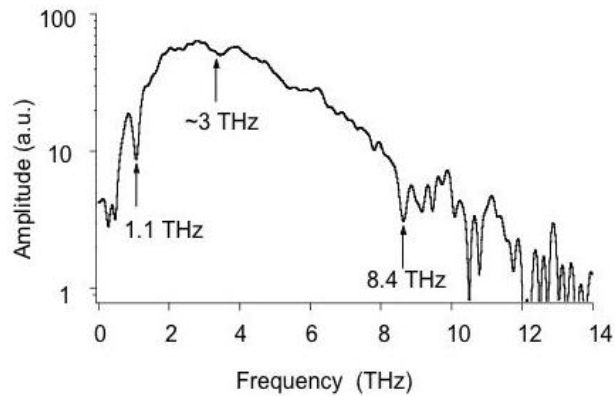


Figure 8. Broadband THz spectrum obtained from the DAST emitter-LAPC sensor pair operated at ~ 1300 nm. The dips marked by the arrows are attributed to the multiple phonon absorption bands in DAST.

With LAPC having the good phase-matching property at ~ 1300 nm, it was interesting to find out how far we can go by simply increasing the interaction length. Therefore, we did experiments on multi-layer LAPC emitters (see Fig. 9) at this wavelength. Surprisingly, the four-layer LAPC emitter did not provide more THz radiation than the three-layer LAPC emitter. This does not agree with our expectation out of the phase-matching study. Tentatively, we think that the disagreement might be due to the THz absorption in LAPC, which we neglected in our theoretical study. It becomes crucial at this point that we understand this issue if we want to make relatively long guided-wave THz emitters.

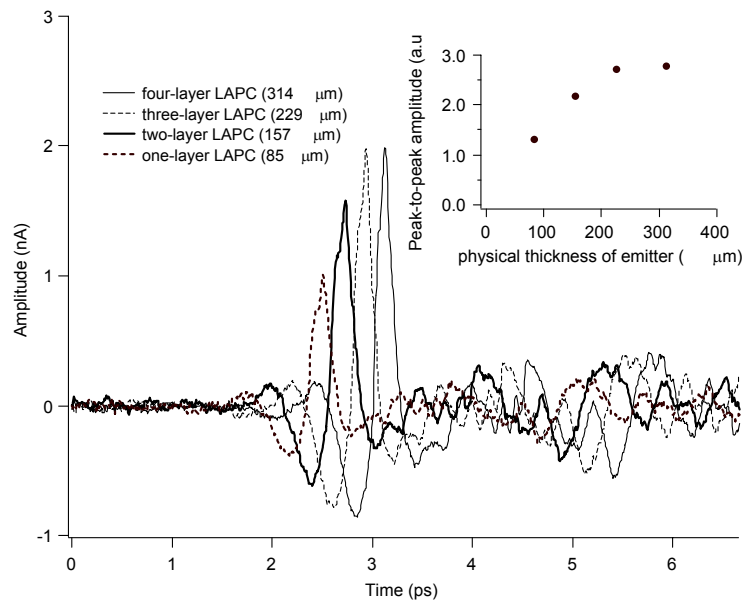


Figure 9. THz waveforms obtained from multi-layer LAPC emitters, measured by a 2-mm ZnTe sensor. All the emitters and sensors are operated at ~ 1300 nm. The inset shows the peak-to-peak amplitude vs. the physical thickness of the emitters.

5. CONCLUSIONS

We have presented our recent research using EO polymers to generate and detection broadband THz radiation. Amorphous EO polymers have high EO coefficients do not have the phonon absorption in the THz regime, making them advantageous over any other EO materials to achieve a broadband THz system free of spectral gaps. We have experimentally demonstrated a spectral gap-free THz system with a useful bandwidth of ~12 THz based on a LAPC emitter-sensor pair. Phase-matching capability of LAPC was carefully investigated via both THz-TDS and THz emission experiments. As a flat THz index over a broad frequency range is a general feature for all amorphous EO polymers, it can be envisioned that the use of an EO-polymer with both a high EO coefficient, low absorption in the optical and THz regime, and a good phase-matching property at a right optical wavelength is going to dramatically improve the performance of a THz system. Developing such an EO polymer is our goal.

ACKNOWLEDGEMENTS

This work is partially supported by the NSF Center on Materials and Devices for Information Technology Research (CMDITR), DMR-0120967.

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