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RESEARCH ARTICLE

Ultrafast photoexcitation dynamics of ZnTe crystals by femtosecond optical pump-probe and terahertz emission spectroscopy

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Abstract

In this work we perform ultrafast optical pump-optical probe (OPOP) and optical pump terahertz (THz) emission (OPTE) studies on the ultrafast excitation dynamics in <110> ZnTe crystals. Ultrafast two-photon absorption and coherent phonon are revealed in OPOP measurements. Pump-power- and polarization-dependent phonon dynamics are characterized in time-resolved transmission, reflection, and Kerr rotation using OPOP. The phonon polariton-induced THz emission is directly observed in the time domain of OPTE dynamics. It is clear that the transverse optical phonon at ~3.7 THz and phonon polariton at ~2.6 THz are evident in OPOP measurement while OPTE only reveals part of the polariton dynamics.

KEYWORDS

pump-probe spectroscopy, terahertz, ultrafast spectroscopy

1 | INTRODUCTION

The wide bandgap semiconductor ZnTe is widely employed as both the detection and generation medium in terahertz-related optical and spectroscopy setups.[1] Due to its wide applications, the ultrafast dynamics and origin of the coherent phonons in ZnTe have been intensely studied and debated over the past decades.[2-9]

The generation, propagation, and detection of coherent optical phonon (COP) have been extensively investigated in solid materials such as semimetals,[10] semiconductors,[11,12] and topological insulators[9,13-17] by ultrafast pump-probe measurements. One mechanism for generating COP by ultrafast optical excitation is the impulsive stimulated Raman scattering.[18] When a femtosecond pulse is tightly focused on a solid sample, the different wave-vector components of the pulse intersect and generate a spatially periodic, temporally impulsive driving force on the phonon mode through stimulated Raman scattering. This impulsive driving force stimulates impulse response of the phonon mode (ie, coherent phonon), which appears as a coherent time-dependent standing-wave oscillation. As a result, the sample's refractive index is modulated, leading to a transient refractive index grating. In polar materials such as $LiNbO_3$ and ZnTe crystal, the femtosecond pulse can create a region of nonlinear polarization via second-order nonlinear optical process, which may act as a source term for terahertz (THz) electromagnetic field. The coupling between a THz field and a transverse optical phonon mode of similar frequency gives rise to a mixed mode, the so-called THz phonon polariton. Both the THz field and the phonon polariton in material can generate free space THz radiation. In ultrafast optical pump-optical probe (OPOP),[19] by measuring the time-resolved changes of the intensity or polarization of probe beam after interaction with the coherent phonon or phonon polariton, the dynamics of phonon modes is detected and its frequency and strength can be extracted from the corresponding fast Fourier transform spectrum.[20–25] In optical pump THz emission (OPTE) measurement, free space THz waveforms are measured with electro-optic (EO) sampling using an EO crystal.

In this work, we experimentally investigate the dynamics of coherent phonon in <110> ZnTe crystal using ultrafast OPOP and OPTE techniques. It is shown that the transverse optical (TO) phonon at ~3.7 THz and phonon polariton at ~2.6 THz are evident in OPOP measurement while OPTE only reveals part of the polariton dynamics. Our work may shed light on understanding the generation and detection of coherent phonon in ZnTe and other II-VI compounds.

2 | EXPERIMENTAL SETUP

The experiment is performed on a home-built OPOP setup as schematically demonstrated in Figure 1A,B. It enables measurements of both transient transmittance (ΔT) and transient reflectivity (ΔR). The transient dynamics is measured at room temperature by employing a femtosecond fiber laser (C-fiber780; Menlo-systems) with a repetition rate of 100 MHz, central wavelength of 780 nm, and pulse duration of ~90 fs. The laser output is split into two beams by a 70:30 splitter. The stronger beam is employed as the pump and the weaker as the probe. A computer-controlled delay stage is used to manipulate the relative time delay between pump and probe. The pump beam is modulated by an optical chopper at 1 kHz. The pump and probe beams are focused into the <110> ZnTe crystal by a lens with focal length 50 mm. The focused laser spot has a diameter of 25 μm. The pump fluence can be adjusted from 2 to 120 $\mu J/cm^2$ with a gradient neutral density attenuator and the probe fluence was fixed at 0.4 $\mu J/cm^2$. Both the reflected and transmitted probe beams are detected by Si photodiode detectors. The Kerr rotation effect is measured by detecting pump-induced changes of the polarization of probe beam with an analyzer (Glan-laser polarizer) in front of the photodiode. For OPTE measurement, THz generation from the ZnTe crystal upon ultrafast optical pump is detected by employing a separate THz time-domain spectroscopy (TDS), as exhibited in Figure 1C.

3 | RESULTS AND DISCUSSION

The −ΔT/T around zero delay time under different pump powers are shown in Figure 2A. The peak value of −ΔT/T increases linearly with the pump power from 1 to 54 mW (corresponding to 2-110 $\mu J/cm^2$), as shown in Figure 2B. The time-resolved ΔR/R with different pump power are also measured and shown in Figure 3A. The dependence of the peak value of −ΔR/R on pump power shows the same trend as the −ΔT/T, as shown in Figure 3B. These results indicate that the transient −ΔT/T and −ΔR/R peaks are the manifestation of a transient absorption process. It can be attributed to two-photon absorption (TPA) in the ZnTe crystal.[4] When pump and probe pulses overlap temporally and spatially at the sample, the sample absorbs one photon from the pump pulse and another from the probe. The strength of this particular TPA process is proportional to the product of pump and probe fluence ($I_{pump} \times I_{probe}$), resulting in the linear dependence on I_{pump}. It should be noted that the pump pulse itself induces a stronger TPA process with a strength proportional to $I_{pump} \times I_{pump}$, which excites more free carriers in the ZnTe. Recent studies have pointed out that the pump-induced free carriers due to TPA may play a role in the ultrafast dynamics of phonons and polaritons, which consequently influence the THz spectroscopy based on ZnTe.[4]

We further measure the dependence of TPA on the polarization of the laser pulses. A zero-order half-wave plate is employed to tune the polarization direction. The angle between the <001> crystal axis of ZnTe and the polarization direction of the laser is labeled as θ, as shown in Figure 4A. The θ-dependent peak values of −ΔT/T are plotted in Figure 4B as the solid circles, which can be well fitted by $y(\theta) = A \times \cos^2\theta$ (red curve). When $\theta = 0°$ or 180°, the ZnTe crystal exhibits intense TPA, while the TPA is suppressed at $\theta = 90°$ or 270°. Therefore, when ZnTe is utilized to generate THz radiation through optical rectification pumped by femtosecond laser pulse, the loss of pump power due to TPA should be handled carefully, as it might hamper the efficiency of THz emission.

Below, we focus on the ultrafast excitation dynamics in ZnTe after the transient TPA peak. When the pump and probe polarizations are parallel to the <001> direction, the $<1\bar{1}0>$-polarized coherent phonon mode at 3.7 THz can be detected as the long damped oscillation tail (LDOT) in the time domain due to impulsive stimulated Raman scattering.[18] ΔT/T time profiles are shown in Figure 5A where periodic oscillations can be clearly observed after the TPA peak. With pump power varying from 1 to 54 mW, the LDOT of the TO phonon in the time domain is always observed. Figure 5B shows the Fourier transforms of the LDOT of the time profiles in Figure 5A. The dominant frequency is determined to be 3.7 THz, which is consistent with the TO phonon frequency previously studied.[9] The pure oscillations after the main peak, after removing the background, can be fitted by $y(t) = Ae^{-t/\tau}cos(\omega t + \phi)$, where τ represents the characteristic phonon lifetime. τ is found to decrease as the pump power increases, as shown in Figure 5C.

The decreasing trend of phonon lifetime with increasing pump power can be ascribed to a combined effect of faster pure dephasing of the phonon mode, increased phonon population decay, and/or elevated crystal temperature.[26] When a large number of free carriers are excited in ZnTe by TPA process, the interaction between COPs and free carriers is significantly enhanced. This interaction can increase the pure dephasing rates of phonon and consequently lead to shorter phonon lifetime.[27] On the other hand, the phonon population decay is also accelerated upon intense excitation, due to anharmonic decay and/or due to additional phonon population decay induced via heating of free carriers by coherent phonons.[28]

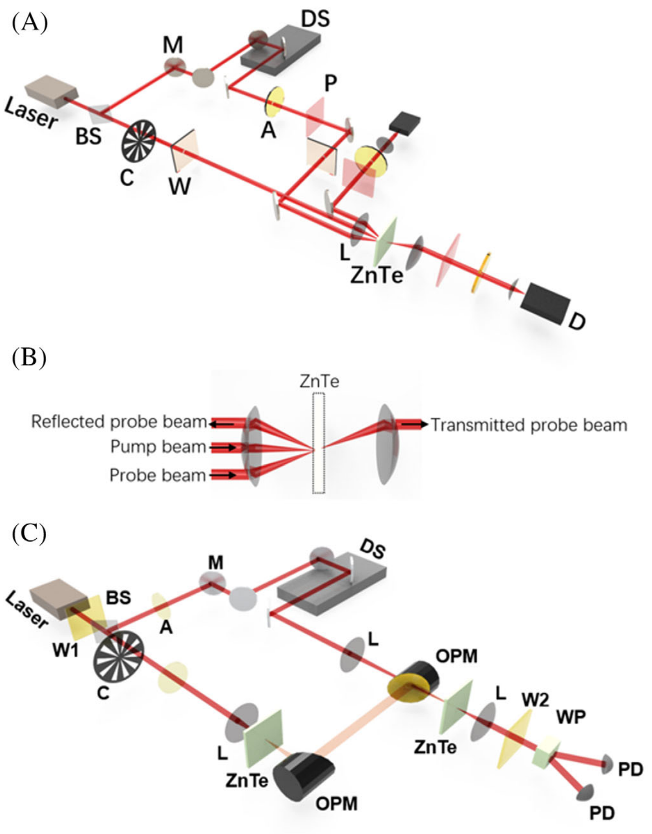

FIGURE 1 A, Schematics of the optical pump-optical probe (OPOP) experimental setup. BS, beam splitter; C, chopper; M, mirror; DS, delay stage; W, half-wave plate; A, attenuator; P, polarizer; L, lens; D, detector. B, A zoom-in view on the sample and focusing optics, indicating incident pump and probe beam, as well as transmitted and reflected probe beam. C, Schematics of the optical pump terahertz emission (OPTE) experimental setup. BS, beam splitter; C, chopper; M, mirror; DS, delay stage; W1, half-wave plate; W2, quarter-wave plate; A, attenuator; P, off-axis parabolic mirror; L, lens; PD, photoelectric detector [Color figure can be viewed at wileyonlinelibrary.com]

When the pump polarization is set parallel while the probe polarization perpendicular to the <001> crystal axis, two oscillation modes can be observed in the transient reflectivity spectra (Figure 6A). A typical Fourier transform of the LDOT as shown in Figure 6B clearly reveals two peaks at 2.6 and 3.7 THz. The 2.6 THz peak is associated with the formation of phonon polariton due to the hybridization of pump-induced THz radiation and the TO phonon in ZnTe.[4,6,8] We found that the phonon and phonon polariton amplitude both increase linearly with pump power up to 60 mW (corresponding to 120 μJ/cm^2), as is shown in Figure 6C. Nonlinear region has yet to be achieved with our pump fluence.

In order to observe the dynamics of phonon polariton more clearly, we performed ultrafast time-resolved optical Kerr effect measurement, which eliminates the interference of coherent TO phonon at 3.7 THz. To study this, the polarizer in front of the detector is set to 90° angle with respect to incident polarization. Transient transmittance time profile under this setting is shown in Figure 7A where LDOT is also observed after the TPA peak (Figure 7B). Fourier transform of the oscillation reveals the dominant frequency at 2.6 THz (Figure 7C).[6]

THz radiation produced through optical rectification by irradiating <110> ZnTe with ultrafast optical pulses usually only consists of few-cycle electromagnetic oscillations about few picoseconds long. However, LDOT can be generated due to the phonon polariton launched by the hybridization of THz radiation and the TO phonon of similar frequency in ZnTe.[6] In this part, we use the same ZnTe crystal as the THz generator in a typical OPTE setup (Figure 1C). Time-domain profile is shown in Figure 8A where strong oscillation (enlarged in Figure 8B) presents after the main peak. Fourier transform of the LDOT shows the central frequency to be at 2.36 THz, which is noticeably lower than previously determined using OPOP (Figures 6 and 7). In a previous report using OPTE, the phonon polariton frequency is found to be between 1.9 and 2.7 THz, depending on the central frequency and the pulse duration of the pump beam.[6] More specifically, 1.9 THz (2.7 THz) corresponds to 800 nm (750 nm) pump. In our experiment 780 nm center

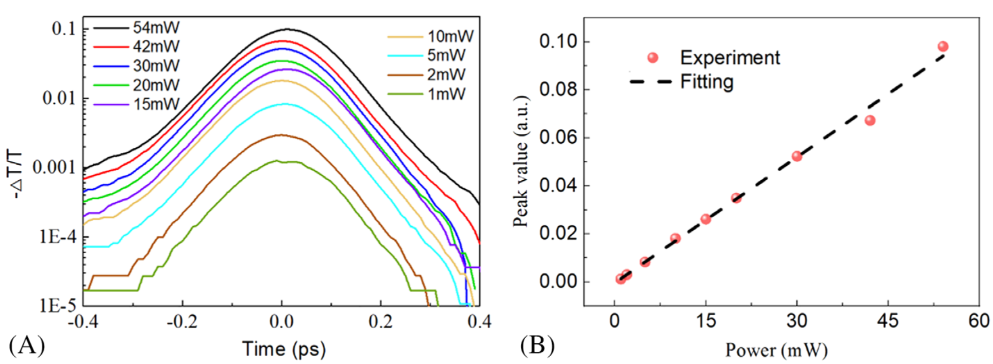

FIGURE 2 A, ΔT/T as a function of time under various pump power. B, ΔT/T peak value dependence on pump power, the linear fitting shows good agreement with experimental data [Color figure can be viewed at wileyonlinelibrary.com]

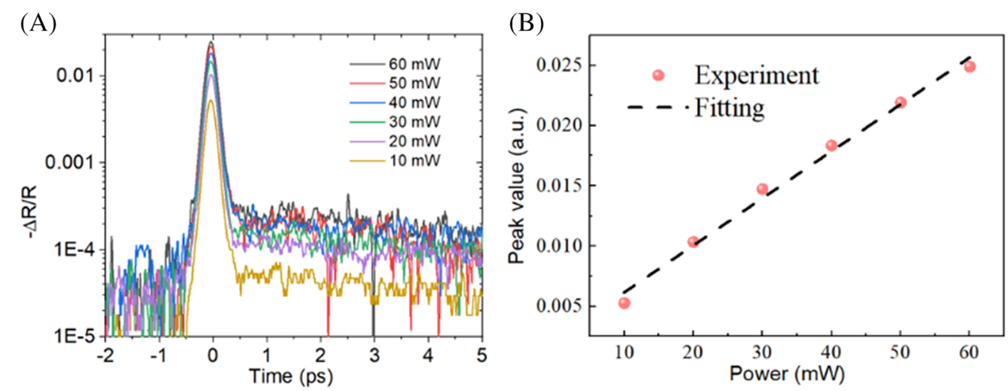

FIGURE 3 A, ΔR/R as a function of time under various pump power. B, ΔR/R peak value dependence on pump power, the linear fitting shows good agreement with experimental data [Color figure can be viewed at wileyonlinelibrary.com]

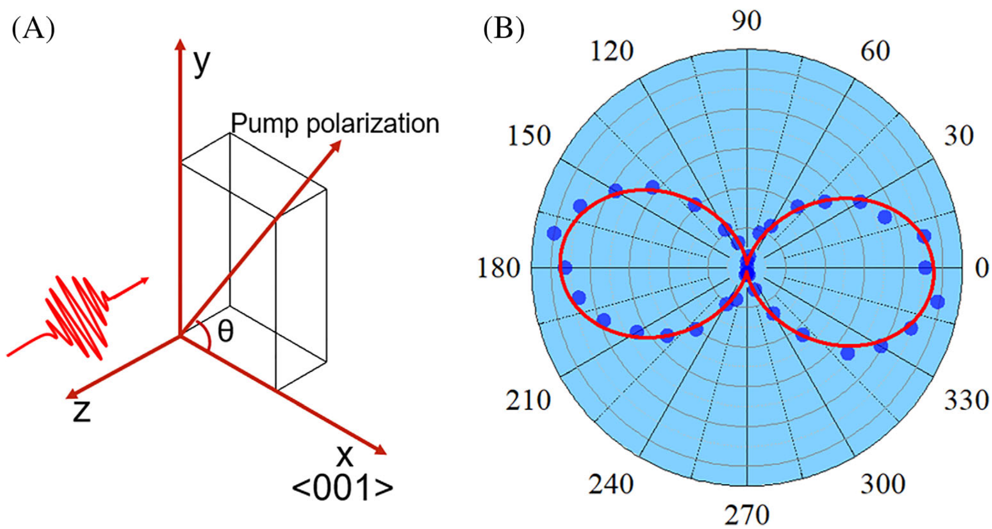

FIGURE 4 A, Schematics of the crystal orientation and incident beam polarization direction. B, −ΔT/T peak value as a function of the angle between <001> crystal axis and pump beam polarization. The black dots are experimental data and the red curve is the $\sin^2\theta$ fit [Color figure can be viewed at wileyonlinelibrary.com]

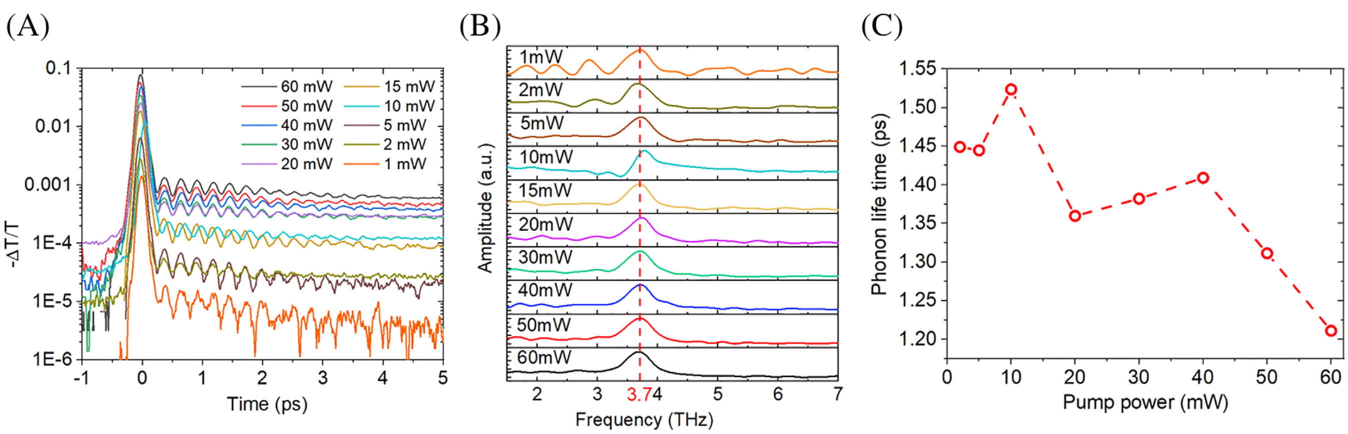

FIGURE 5 A, ΔT/T as a function of time under various pump power. B, Fourier transforms of oscillations after the main peak in A, a peak at 3.7 THz is clearly observed, consistent with previously observed phonon frequency. C, Change of phonon lifetime with respect to pump power. The decreasing trend of phonon lifetime can be attributed to stronger damping induced by photoexcited free carriers and higher temperature with rising pump power. THz, terahertz [Color figure can be viewed at wileyonlinelibrary.com]

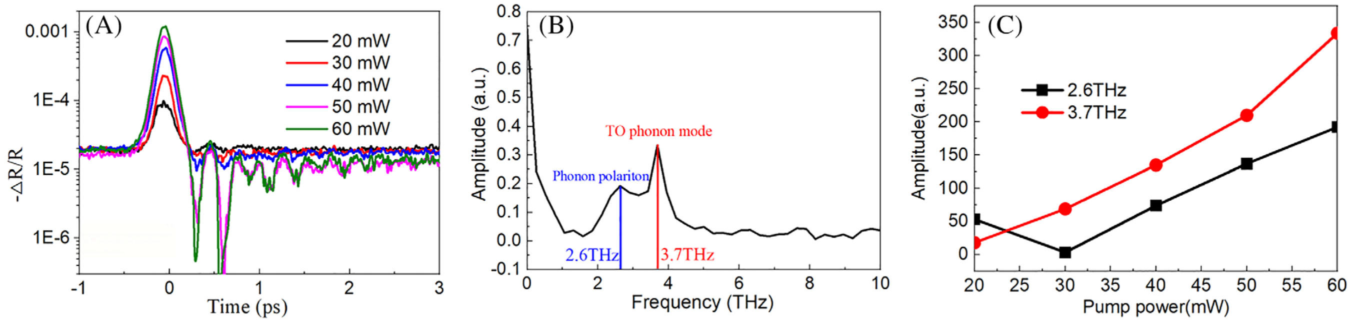

FIGURE 6 A, ΔR/R as a function of time under various pump powers. Oscillations after the main peak are clearly observable. B, Fourier transform of the oscillation after the main peak removed. The phonon polariton at 2.6 THz and transverse optical (TO) phonon mode at 3.7 THz can be obtained at the same time. C, Change of ΔR/R peak value with various pump power for phonon polariton (2.6 THz) and phonon (3.7 THz), both increasing linearly with pump power. THz, terahertz [Color figure can be viewed at wileyonlinelibrary.com]

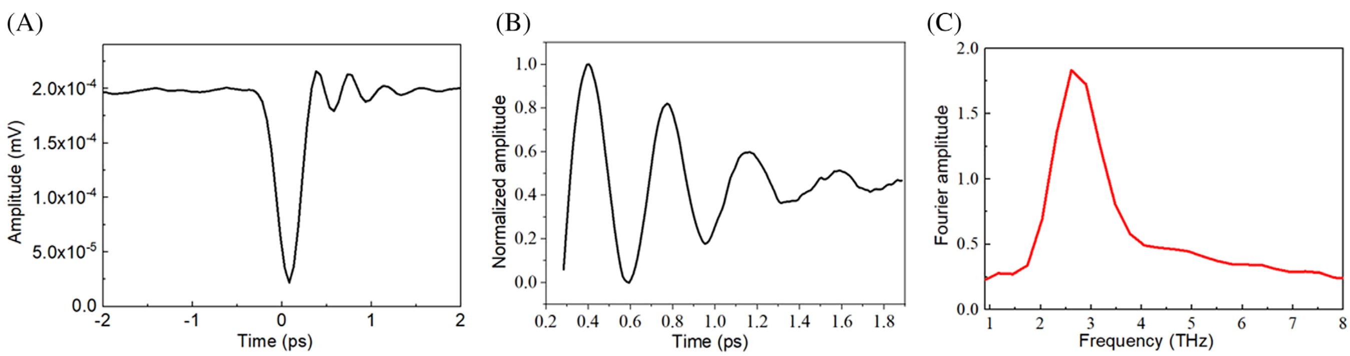

FIGURE 7 A, Detected Kerr effect signal as a function of time under the pump power of 20 mW. B, Oscillations after the main peak extracted from A. C, Fourier transform of B, showing a peak at 2.6 THz. THz, terahertz [Color figure can be viewed at wileyonlinelibrary.com]

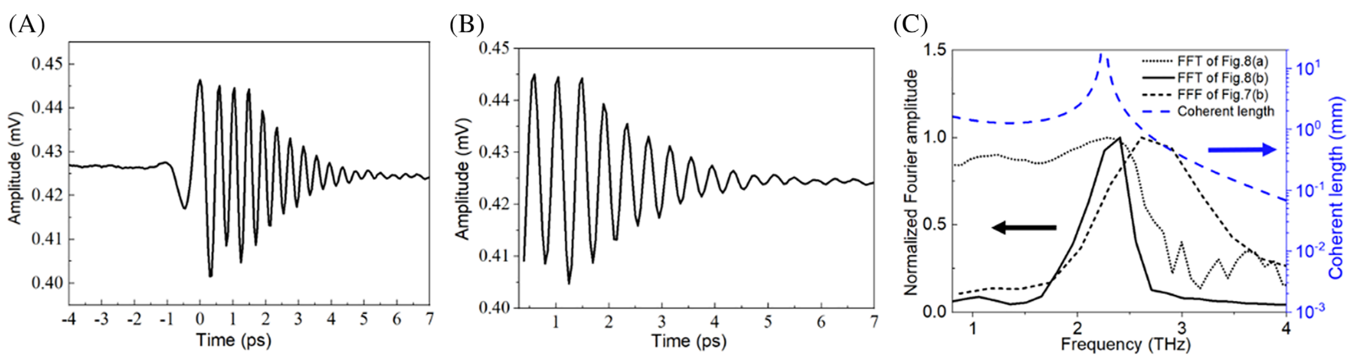

FIGURE 8 A, Terahertz waveform in the time domain. B, Oscillations after the main terahertz peak removed from A. C, Fourier transforms of Figure 8A,B, and Figure 7B, showing the peak frequency difference and the weight lost at high frequency observed in optical pump-optical probe (OPOP). The coherent length is also plotted, which explains the peak frequency difference and weight loss [Color figure can be viewed at wileyonlinelibrary.com]

wavelength is used, which leads to the probing of phonon polariton frequency centered at 2.36 THz. We calculated the coherence length (l_c) between the pump pulse and different frequency components of THz radiation and found that the phase matched frequency, determined by $l_c \rightarrow \infty$, for the 780 nm pump is around 2.2 THz. Figure 8C shows the Fourier transforms of the full pulse in Figure 8A and LDOT in Figure 8B compared to that in the Kerr rotation spectrum (Figure 7B). The difference in the peak frequency and width is evident. The missing spectral weight from the OPTE (compared to the Kerr rotation spectrum) is due to the small coherence length between the optical beam and the THz frequency modes. The coherence length calculated according to References 8 and 29 is shown in Figure 8C.

4 | CONCLUSION

In this article, a multifacet experimental study of the ultrafast dynamics in ZnTe crystal is carried out using OPOP and

OPTE techniques. The <$1\bar{1}0$>-polarized TO phonon mode at 3.7 THz and phonon polariton mode at 2.6 THz can be identified in LDOT of the OPOP time-domain spectra. However, OPTE reveals a LDOT centered around 2.36 THz, which we attribute to the small coherent length between the optical and THz pulses beyond ~2.4 THz.

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