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# Indication of Te segregation in laser-irradiated ZnTe observed by *in situ* coherent-phonon spectroscopy

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We irradiate a ZnTe single crystal with 10-fs laser pulses at a repetition rate of 80 MHz and investigate its resulting gradual modification by means of coherent-phonon spectroscopy. We observe the emergence of a phonon mode at about 3.6 THz whose amplitude and lifetime grow monotonously with irradiation time. The speed of this process depends sensitively on the pump-pulse duration. Our observations strongly indicate that the emerging phonon mode arises from a Te phase induced by multiphoton absorption of incident laser pulses. A potential application of our findings is laser-machining of microstructures in the bulk of a ZnTe crystal, a highly relevant electrooptic material.
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The fabrication of micrometer-sized structures in optical materials has a wide range of applications, for instance, in integrated microoptics,[1] biophotonic devices,[2,3] mechanical vibrational sensors,[4] and optical three-dimensional data storage.[5] Examples of microoptical devices include surface gratings[6] and microchannel waveguides.[7,8] A successful route toward preparation of these structures is based on optical multiphoton absorption using femtosecond laser pulses. When such pulse is focused onto a transparent sample, the nonlinear response can lead to physical processes like avalanche ionization, plasma formation and micro-explosions.[9–11] It was found that for the fabrication of low-loss microchannel waveguides at faster writing speeds ($>1\,\mathrm{mm\,s^{-1}}$), pulse trains with elevated repetition rates ($>200$ kHz) are even more adequate due to accumulative heating that enhances localized melting.[8] More specifically, high repetition rates were shown to be ideal for fabricating three-dimensional waveguide structures in transparent crystalline materials like $LiTaO_3$.[12] It is highly desirable to extend this powerful method to other technologically relevant materials.

One of such materials is ZnTe, a II-VI semiconductor with a band gap of 2.24 eV.[13] It is one of the most commonly used materials for the laser-based generation and detection of terahertz (THz) electromagnetic waves.[14] With two atoms per elementary cell, ZnTe has three optical phonons at the center of the Brillouin zone, namely a doubly degenerate transverse-optical (TO) mode at 5.31 THz and a longitudinal-optical (LO) mode at 6.24 THz.[13] Apart from these zone-center resonances, infrared spectroscopy revealed two modes at 1.6 and 3.6 THz.[15–17] The 3.6-THz resonance was also observed in coherent-phonon spectroscopy,[18–20] but its origin is still a matter of debate.[16–20] Note that ZnTe has a relatively large cross section for two-photon absorption (TPA),[21,22] which limits its efficiency for THz wave generation.[23] This drawback, however, might turn into a benefit in terms of material modification using femtosecond laser pulses.

In this letter, we show that 80-MHz trains of 10-fs, 800-nm laser pulses can be used to induce permanent modifications in crystals of semiconducting ZnTe. The laser-induced changes are accompanied by the gradual manifestation of a mode at 3.6 THz in the coherent-phonon spectrum, and we assign this mode to the formation of a Te phase. Our results are relevant for implementing laser-based machining of ZnTe. In addition, this investigation will help settle the controversy[16–20] on the origin of a 3.6-THz mode that is frequently observed in ZnTe.

The sample investigated is a 440-$\mu$m-thick single crystal of ZnTe(110). In our setup, the output of a femtosecond Ti:sapphire laser oscillator (pulse duration of 10 fs, center wavelength of 800 nm, repetition rate of 80 MHz) is split into two beams, a pump (power of 210 mW) and a probe beam (40 mW). Both beams are focused onto the sample surface, the pump under normal incidence and the probe at approximately 10° with respect to the surface normal, resulting in beam diameters (half width at 1/e maximum) of 22 and 19 $\mu$m, respectively.

The pump beam has two purposes: gradual sample modification and launching coherent lattice vibrations for studying these modifications. The coherent-phonon dynamics is monitored by the probe pulse, which measures the transient optical anisotropy of the sample as a function of the delay $\tau$ between pump and probe pulses. Because of this anisotropy, the initially linearly polarized probe becomes elliptically polarized characterized by the ellipticity $S$, the ratio of the small and the large amplitude axis of the polarization ellipse. We detect $S$ by using a combination of a quarter-wave plate, a polarizing beam splitter and two balanced photodiodes.[24] The pump-probe delay $\tau$ is varied by periodically modulating the length of the probe path at a frequency of 15 Hz using a so-called shaker. As soon as the pump is allowed to irradiate the sample, data are recorded up to 35 min in averaging

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intervals of 2 s. All measurements are performed under ambient conditions in air.

The choice of pump and probe polarizations deserves a detailed comment: they are set such that no pump-probe signal from ZnTe-intrinsic coherent optical phonons nor from pump-generated THz radiation can occur. The pump polarization is chosen linear and set parallel to the $\langle 001 \rangle$ direction, thereby preventing optical rectification and excitation of the LO phonon and $\langle 001 \rangle$-polarized TO modes.[19,25,26] However, the other, $\langle 1\bar{1}0 \rangle$-polarized TO mode is excited, yet by setting the probe polarization to an angle of 45° with respect to the pump polarization, the probe will experience a fully isotropic response, resulting in a vanishing ellipticity signal.[18,19,26]

Figure 1(a) displays as-recorded ultrafast pump-induced changes in the sample anisotropy after pump exposure times of 0, 7, and 30 min. Signals $S(\tau)$ are seen to consist of a slowly varying background, a (negative) peak around zero delay and an oscillatory part [Fig. 1(a)]. The slowly varying signal background is an artifact arising from the slightly elliptical motion of the shaker. Remarkably, the height of the zero-delay peak decreases in the course of sample irradiation, whereas the amplitude and lifetime of the oscillation exhibit a strong increase.

The initial peak most likely arises from an instantaneous interaction of pump and probe pulses such as the optical Kerr effect or TPA,[19,22,27] in which one pump and one probe photon drive an optical transition across the ZnTe band gap of 2.24 eV[13] simultaneously, when both pulses overlap.

We identify the oscillatory part of $S$ with a coherent lattice vibration, as electronic resonances at THz frequencies have not been reported for ZnTe. To separate this contribution from the transient signal, we apply a band-pass filter to $S(\tau)$ and truncate the signal for pump-probe delays below 0.42 ps. The resulting waveforms and their Fourier transformations are shown in Fig. 1(b) (gray lines) and Fig. 1(c), respectively. Directly after illumination has started (0 min), the time-domain data exhibit only very weak oscillations [Fig. 1(b)]. The amplitude spectrum [Fig. 1(c)] contains a broad feature centered at 3.2 THz. A small and relatively sharp peak at 6.3 THz arises from the ZnTe-intrinsic LO phonon at 6.24 THz,[13] which is not fully suppressed in our experiment. Remarkably, after 7 min of illumination, a distinct oscillation is found in the raw [Fig. 1(a)] and filtered [Fig. 1(b)] time-domain data. Indeed, the resulting Fourier amplitude spectra [Fig. 1(c)] indicate the emergence of a new mode at 3.6 THz. At 30 min, the oscillation amplitude has increased further [Fig. 1(b)], and the width of the spectral peak [Fig. 1(c)] has narrowed, implying a longer lifetime.

To quantify the temporal development of this mode, we fit the lattice vibration [Fig. 1(b)] by an exponentially damped harmonic oscillation according to

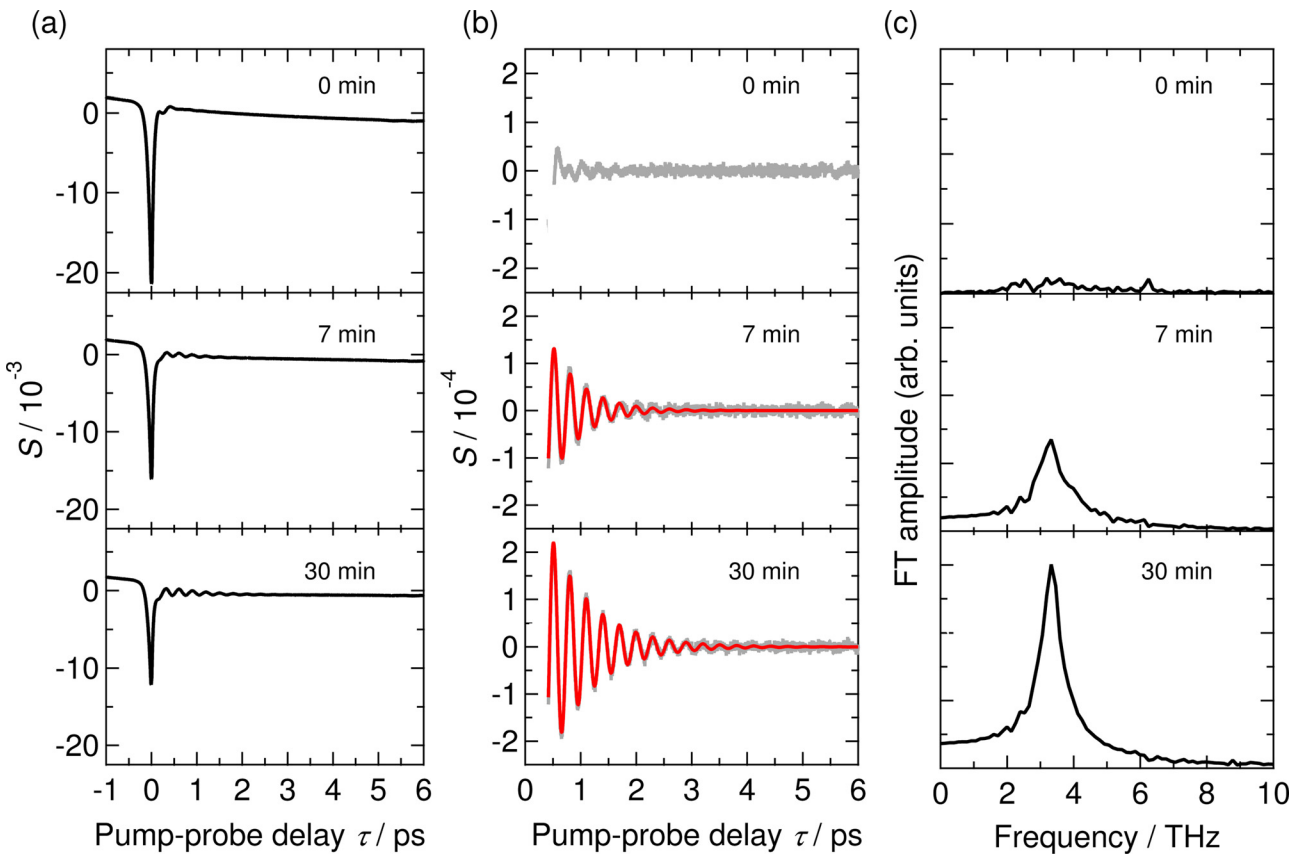


FIG. 1. Coherent-phonon spectroscopy data of a laser-illuminated ZnTe(110) crystal. (a) As-recorded ultrafast dynamics of the probe-pulse ellipticity $S$ reflecting the transient anisotropy induced by excitation with femtosecond laser pulses. The traces are obtained following laser irradiation times of 0, 7, and 30 min, respectively. Note the gradual emergence of an oscillatory component. (b) Oscillatory part of the traces of panel (a) obtained by band-pass filtering and truncating data at pump-probe delays <0.42 ps (gray). Red solid curves are fits using Eq. (1). (c) Fourier amplitude spectra of the traces of panel (b).

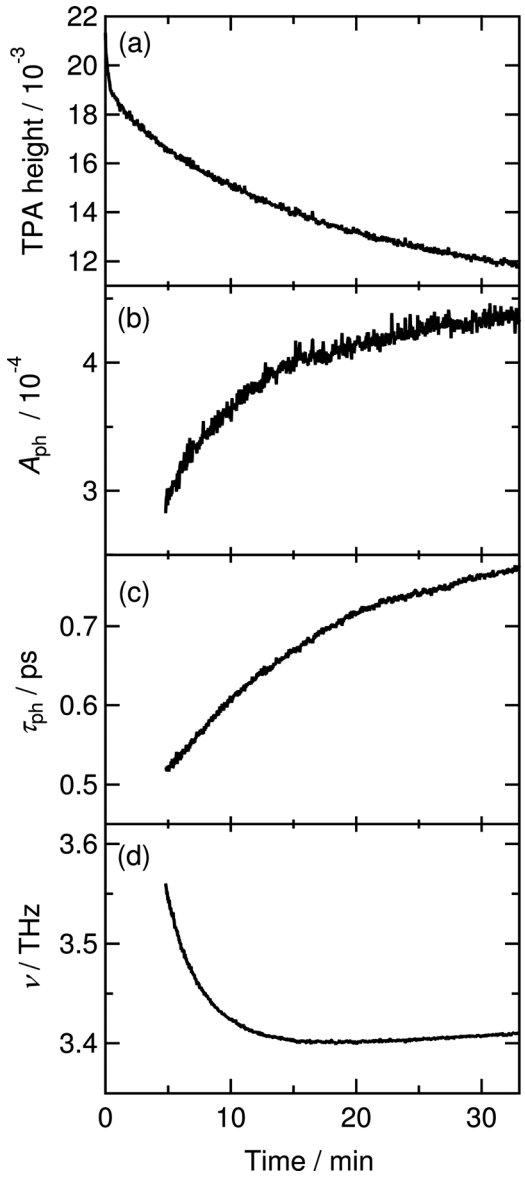


FIG. 2. Variation of parameters extracted from the time-domain signals of Fig. 1 as a function of laser irradiation time. (a) Height of the peak around zero delay, (b) amplitude $A_{ph}$ of the coherent phonon as well as its (c) lifetime $\tau_{ph}$ and (d) frequency $\nu$.

$$S(\tau) = A_{ph} \exp\left(-\frac{\tau}{\tau_{ph}}\right) \sin(2\pi\nu\tau + \phi). \quad (1)$$

Here, $A_{ph}$ is the amplitude of the coherent phonon, $\tau_{ph}$ its lifetime, $\nu$ its frequency, and $\phi$ its initial phase. The resulting fits [red curves in Fig. 1(b)] are in good agreement with the measured data. Figure 2 shows the temporal evolution of the three fit parameters along with the height of the peak around $\tau = 0$. Data start after 5 min of ZnTe irradiation, because reliable fits are not possible for shorter exposure times. While the zero-delay peak height is found to decrease by about 40% over an exposure time of 30 min, the amplitude $A_{ph}$ and lifetime $\tau_{ph}$ of the coherent phonon are found to increase by about 60%. The phonon frequency $\nu$ starts at 3.55 THz and then approaches a value of 3.4 THz by 30 min.

We emphasize that these frequencies do not at all coincide with any of the three zone-center optical phonons of ZnTe (see above[13]). Instead, we suggest that the development of the laser-induced phonon mode reflects the gradual formation of an at least partially crystalline Te phase induced by multiphoton absorption of the incident pump laser. This notion is substantiated by the following arguments.

First, crystalline Te has a Raman-active, totally symmetric $A_1$ mode at a frequency of 3.6 THz,[28,29] which agrees quite well with the resonance frequency observed in our experiment at 5 min after starting irradiation [Fig. 2(d)]. The subsequent frequency decrease down to 3.4 THz most likely arises from laser-heating of the sample volume probed. Such thermal red-shift has been observed previously in pump-probe experiments on Te and was assigned to bond weakening by excited electrons.[30–32] We note that despite being totally symmetric, the $A_1$ mode leads to an anisotropic transient optical response.[31] The reason is that Te is itself optically birefringent, owing to its hexagonal lattice structure. As a consequence, to generate a nonvanishing anisotropic signal as seen here, the segregated Te phase must exhibit a certain degree of crystalline order.

Second, Te segregation due to continuous-wave laser illumination (photon energy above band-gap energy) was already observed for various semiconductors, including ZnTe epilayers[33] and crystals of CdZnTe,[34,35] $CuInTe_2$,[36] $CdIn_2Te_4$, $ZnIn_2Te_4$, and $MnIn_2Te_4$.[37] Te segregation induced by laser pulses (200 fs, 1580 nm) was observed in $Sb_2Te_3$ films.[38] It has to be noted that neither in our work nor in previous works on Te segregation in Zn-containing solids,[33–35,37] Raman signatures of the concomitantly proceeding Zn separation were detected. One reason for this lack of a Zn signal is most likely that the Raman tensor of the $E_{2g}$ phonon of Zn is about an order of magnitude smaller than that of the $A_1$ mode of Te, as one can infer by comparing coherent-phonon works on Zn[39] and Te.[30]

We emphasize that in previous experiments on laser-induced Te segregation,[33–38] the optical excitation was across the electronic band gap of the semiconductor. In the present study, the pump photon energy (1.55 eV) is well below the ZnTe band gap (2.24 eV).[13] Since Te formation requires deposition of optical energy, Te segregation must be initiated by TPA or, more generally, multiphoton absorption of pump light. This notion is confirmed by the following qualitative observation. After stretching the pump pulse to a duration of about ≈30 fs using a 2-mm-thick window of BK7 glass, the experiment was repeated. We did not observe any measurable signature of the coherent-phonon mode at 3.6 THz over an illumination time of 30 min.

The kinetics of laser-induced Te segregation (as reflected by Fig. 2) is probably a complex process, and its understanding requires further studies. For example, once Te segregation has started, the newly formed Te phase will dissipate additional pump radiation by one-photon absorption, possibly leading to additional heating and, in turn, accelerated Te formation.

We finally note that the resonance at ≈3.6 THz observed here was already seen in previous spectroscopy works on ZnTe, but assigned to more complex, intrinsic modes, namely a difference mode TO(X)–TA(X) between a TO and transverse-acoustic (TA) phonon,[17,18] a longitudinal-acoustic mode,[16,19] and a two-phonon bound state.[20] Our present results suggest that all these studies may have addressed the same 3.6-THz mode of a Te phase in ZnTe crystals, either

laser-induced or already preexisting.[40] This view is corroborated by a previous temperature-dependent study of this mode in a low-purity ZnTe crystal that provided evidence that this mode is a one-phonon state,[19] consistent with the temperature-dependence of the $A_1$ mode in Te.[32]

In conclusion, we have monitored the gradual emergence of a phonon mode at ≈3.6 THz in ZnTe crystals irradiated with femtosecond laser pulses. Our results strongly indicate that the new lattice mode arises from the laser-induced formation of an at least partially crystalline Te phase. Since below-gap excitation requires TPA or, more generally, multiphoton absorption, material modification can happen in ZnTe sample regions much deeper than the penetration depth ($<1\ \mu$m) of above-gap light. Therefore, our observations are potentially interesting for laser-based fabrication of optical microstructures in the bulk of this highly relevant material in electrooptics.

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