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Time-resolved, nonequilibrium carrier and coherent acoustic phonon dynamics in (Cd,Mg)Te single crystals for radiation detectors

John Serafini,[1,2] A. Hossain,[3] R. B. James,[3,4] S. B. Trivedi,[5] and Roman Sobolewski,[1,6,a]

[1]Department of Physics and Astronomy and Laboratory for Laser Energetics
University of Rochester, Rochester, NY 14627-0231, USA
[2]Department of Microsystems Engineering, Rochester
Institute of Technology, Rochester, NY 14623, USA
[3]Brookhaven National Laboratory, Upton, NY 11973-5000 USA
[4]Savannah River National Laboratory, Aiken, NY 29803, USA
[5]Brimrose Technology Corporation, Sparks, MD 21152, USA
[6]Department of Electrical and Computer Engineering and Laboratory for Laser Energetics
University of Rochester, Rochester, NY 14627-0231, USA

Abstract

We present time-resolved nonequilibrium carrier and coherent acoustic phonon dynamics in (Cd,Mg)Te single crystals intended for detection of high-energy x-ray photons. Our (Cd,Mg)Te crystals were grown using a vertical Bridgman method and during the process were doped either with In (a shallow dopant) or Ge (a deep impurity). Next they were cut into platelets and, subsequently, tested as as-grown specimens, or, before testing, long-term annealed in a temperature range of 750 to 800 °C to improve their crystalline properties. All samples exhibited high resistivities of 10^9-10^{10} Ω-cm, as required for x-ray detection applications. We have performed femtosecond optical spectroscopy, pump-probe measurements on all samples in both one-color (high-intensity 800 nm pump and low-intensity 800 nm probe) and two-color (high-intensity 400 nm pump and low-intensity 800 nm probe) configurations, and analyzed results using our carrier-dynamics rate-equation model. The model allowed us to perform a comprehensive, time-resolved analysis of relaxation dynamics of photo-excited carriers and investigate the role of carrier traps present in all tested samples. Two-color measurements also allowed us to observe and analyze propagation of acoustic coherent phonons excited by the high-energy pump pulse. We observed that the dependence of phonon mode frequency, after including a correction of the experimentally measured crystal index of refraction dependence on the probe wavelength, was dispersionless and led to the value for the sound velocity of 3367 m/s, which is in excellent agreement with the literature data. The intrinsic lifetime of coherent phonons in (Cd,Mg)Te was estimated to be on the order of 10 nm. Finally, we conclude that among our tested samples, the In-doped, annealed (Cd,Mg)Te crystal exhibits the best characteristics for radiation detection applications.

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[a]Also at the Institute of Electron Technology, PL-02668, Warszawa, Poland.

1. Introduction

Volume-type radiation detectors are devices that collect charged particles such as electrons, produced by photon interaction with the detector material, typically a single crystal. In the case of highly energetic X-ray radiation photons, they interact with matter through 3 main mechanisms: the photoelectric effect, the Compton effect, and electron-positron pair production. The photoelectric effect is by far the most dominant effect among them, because Compton scattered photons and high-energy gammas from electron-positron pair annihilations typically escape from the detection volume and their energy cannot be collected. Photoconductive devices are, in fact, the most popular solid-state radiation detectors since they can often operate at room temperature, cover the spectral range up to hard X-rays and even γ-rays, and are easy to design and fabricate.

There is a high demand for solid-state X-ray detectors in applications ranging from medical imaging, to homeland security (portable screening units) and astrophysics. Currently, cadmium zinc telluride [(Cd,Zn)Te or CZT] is the accepted material of choice; however due to its large Zn segregation constant it has poor crystal-growth yield making it costly to fabricate in large volumes [1, 2]. Proposed alternatives to CZT are cadmium manganese telluride [(Cd,Mn)Te or CMnT] single crystals [3, 4] and most recently developed cadmium magnesium telluride [(Cd,Mg)Te or CMgT] [5]. The latter material is a ternary alloy as others, but it possesses all of the necessary qualities for an optimal radiation detector, i.e., high density (5.83 g/cc), high effective mass (49.5), high resistivity (~10^{10} Ω-cm), and good electron mobility lifetime ($\mu\tau_e$) product (>10^{-4} cm^2/V) [5]. In addition, the main advantage of CMgT over CZT and CMnT is that its "parent" crystals, CdTe and MgTe, exhibit very similar lattice constants, namely, 6.48 Å and 6.42 Å, respectively [6], resulting in high crystallinity yield of the CMgT material.

Independently, II-VI, Te-based crystals have a variety of very interesting electronic, optical, and magnetic (CMnT) physical properties. They have also been widely implemented as ultrafast photodetectors for the THz-to-ultraviolet (UV) light radiation. CdTe and ZnTe, due to their electro-optic properties, are commonly used as generators and detectors of THz radiation bursts [7, 8]. Presence of magnetic Mn ions in CMnT turns this crystal into a magneto-optic material, exhibiting a giant Faraday effect [9] and, subsequently, a promising compound for ultrafast spintronics and magneto-optics [10, 11], as well as femtosecond electro-optics [12]. Finally, the combined photoconductive (due to ultrahigh resistivity) and electro-optic effects in both CMgT and CMnT single crystals make them materials of choice for "experiment-on-chip" measurements for future ultrafast characterization of various novel materials and devices [13, 14].

This paper focuses on the ultrafast optical properties of the latest member of the above-mentioned ternary materials, namely, the CMgT single crystal. We present comprehensive femtosecond pump-probe spectroscopy studies, where we measure time-resolved carrier dynamics and, subsequently, analyze the data within a coupled rate-equation model, developed to reveal both the carrier recombination and trapping components of the relaxation process. In addition, we time-resolve, long-lived coherent acoustic phonons (CAPs) in a manner similar to a method earlier

implemented for CMnT crystals [15]. In our experiments, we test CMgT crystals with optimal composition and ultrahigh resistivity for X-ray detection applications [16], namely $Cd_{0.92}Mg_{0.08}Te$, and with two different dopants: indium (CMgT:In) and germanium (CMgT:Ge). In both cases the resulting crystals are highly resistive; however, the used dopants act very differently. Indium doping is intended to simply compensate the native concentration of holes (CdTe-based crystals are naturally *p*-type semiconductors), while Ge is a deep impurity, introduced to "pin-down" the Fermi level at the middle of the bandgap. Both sample types are also subject to different post-growth processing–we study both as-grown and annealed crystals. The latter ones are expected to have improved crystalline structure that is visible in our analysis of the density of trap states, presented in Sec. 3.

The structure of the paper is as follows. The next section briefly describes the growth process of our crystals, as well as their optical characterization. Section 3 presents femtosecond pump-probe characterization of our samples, as well as compares experimental results to the carrier relaxation, rate-equation model. Section 4 is devoted to our CAP studies and illustrates how the crystal quality affects the probe-light penetration and the CAP propagation dynamics. Finally, Sec. 5 offers conclusions, as well as some direction for optimizing parameters of CMgT crystals for X-ray detection.

2. (Cd,Mg)Te single-crystal growth and characterization

2.1. Growth technique of CMgT single crystals

Our CMgT:In samples were chosen from as-grown and annealed crystals that were grown using a vertical Bridgman method described by Hossain *et al*. [5]. Subsequently, the ingots were cut into platelets–5x5x2 mm^3–and they were mechanically polished with 800-grit and 1200-grit Al_2O_3 abrasive papers, followed, successively, by 3- and 1-μm, alumina powders. Afterward, all polished surfaces of the samples were chemically etched with a bromine-based solution to diminish polishing damages and to generate clean and smooth surfaces. The sample orientations, determined by X-ray diffraction studies, were (110) and (111) for as-grown and annealed crystals, respectively. The tested crystals exhibited resistivities of 10^9-10^{10} Ω-cm using a 2-probe technique.

CMgT:Ge crystals were also grown by a vertical Bridgman technique. The concentration of Ge in the tested crystals was $1x10^{19}$ atoms/cm^3. After the crystal growth was completed, the crystal was carefully removed from the growth ampoule, and cleaved to expose its (110) cleavage plane. The selected sample was cut into a rectangular shape 10x10x1 mm^3, and ground and polished to an optical finish. The resistivity of the sample was measured to be 3.6×10^{11} Ω-cm using a 2-probe technique.

Annealing of our CMgT:In and CMgT:Ge samples was performed in a horizontal furnace with an isothermal profile at a temperature range of 750 to 800 °C, for 3-5 days, depending upon the thickness of the samples. The process was carried out under Cd over pressure in the range 3-5 torr

(about 0.001 to 0.005 atm). This pressure prevented loss of the sample material during annealing via sublimation.

2.2 Optical bandgap measurements

One important task of this paper is to resolve the differences between the as-grown and annealed CMgT specimens. Thus, we started our sample characterization with absorption spectra measurements performed using a Perkin-Elmer Lambda 900 spectrometer at normal incidence with a scanning wavelength range of 730-to-855 nm. Figure 1 presents our results in the form of a Tauc plot [17]. Each spectrum exhibits a rapidly decreasing segment that signifies the optical absorption edge. By extrapolating this linear region to the x-intercept we can determine the optical bandgap E_G of our material. We note that the annealed CMgT:In sample exhibits the largest E_G = 1.62 eV, while the E_G for the as-grown material is slightly suppressed and equal to 1.61 eV. As expected, these results are in close agreement with [5]. For both as-grown and annealed CMgT:Ge crystals, E_G lies around 1.6 eV. However, the latter spectra, exhibit steeper optical transitions as compared to the In-doped samples. The difference can be explained, as we stress below, by the different roles that the Ge and In impurities play in the CMgT material. We note that the nominal E_G of $Cd_{0.92}Mg_{0.08}Te$ crystals is 1.64 eV [18].

The other striking feature of the spectra shown in Fig. 1 is clearly visible presence of a sub-gap region of non-zero absorption, or, so-called, a band edge tailing, in a roughly defined energy range between 1.53 and 1.6 eV. The only exception is the CMgT:In annealed sample, where the band edge tailing is much more limited. The same sample, as we pointed out earlier, also exhibits the largest E_G value. Based on the absorption spectra, we can conclude that for CMgT:In specimens, annealing significantly reduces the concentration of sub-bandgap states and increases the E_G value, while the impact of annealing on CMgT:Ge crystals is limited only to the E_G enhancement. Indium is a shallow donor used to compensate the native concentration of holes existing in all intrinsic CdTe-based crystals and its presence in band edge tailing is, in general, less pronounced [19, 20]. On the other hand, the Ge dopant [Fig. 1(b)] is a deep impurity that introduces mid-gap trap states [21, 22]; thus, as we see in Fig. 1, the annealing process does not reduce the band edge tailing states. However, it improves the overall crystalline structure CMgT:Ge specimen leading to the increased sharpness of the optical transition.

2.3 Ellipsometry measurements

Ellipsometry studies of our samples were performed using a Woollam W-VASE ellipsometer and the tests were conducted in the 300-1100-nm wavelength λ range at multiple incident angles. The software used to perform modeling of the experimental data was GenOsc® developed by W-VASE and the modeling was optimized with a general oscillator layer acting as a substrate. Fig. 2 presents the index of refraction n dependence on λ for as-grown and annealed CMgT:In crystals (red and blue dots, respectively). We note that for the as-grown sample, the $n(\lambda)$ function has a ~4% larger value at the maximum, as compared to the annealed one. Simultaneously, their maxima are

positioned at λ = 775 nm and λ = 765 nm, for the as-grown and annealed sample, respectively, which corresponds exactly to the E_G values of these samples extrapolated from the Tauc plot (see Fig. 1). Below E_G, with the increase of λ, both $n(\lambda)$ dependencies decrease following the Schubert law [23], as it is indicated by solid black lines. The fits to the Schubert law enabled us to extract the sound velocity in each crystal, equal to ~3040 m/s and ~3370 m/s, for as-grown and annealed CMgT:In crystals, respectively. As we will see in Sec. 3.4, the latter values agree very well with the values obtained from CAP measurements. The $n(\lambda)$ plots for our CMgT:Ge crystals were qualitatively very similar and are not shown here.

3. Femtosecond pump-probe spectroscopy experiments

3.1. Experimental one- and two-color setups

We have implemented two variations of the standard, femtosecond pump-probe spectroscopy technique [24]. In the one-color experiment, a train of 100 fs-wide optical pulses with λ = 800 nm and repetition rate of 76 MHz, generated by a Ti:sapphire laser, was split by a 60/40-beam splitter. The pump beam was modulated with an acousto-optic modulator with the reference frequency set to 100 kHz; while the probe pulses, directly generated by the laser, were delayed with respect to the pump pulses by passing them through a computer-controlled delay stage and aimed near normal incidence to the sample. Both beams were focused on the same spot of the sample (pump down to 30 μm in diameter and probe ~20 μm in diameter) and the pump-to-probe average power ratio was set to at least 10:1, with the probe power set at the 1-mW level (13 pJ of energy per pulse) to minimize probe-related optical heating and, simultaneously, ensure a good signal-to-noise ratio. The probe light reflected off the surface and was captured by a photodetector connected to a lock-in amplifier. Coherent artifact is a well documented issue for this setup [25] and, so, to reduce this effect the beam polarizations were set orthogonal to each other using a half-wave plate and polarizer. The one-color setup has been used to study CMgT:In samples and the selected 800-nm wavelength (energy 1.55 eV) corresponds to photon energies below the nominal E_G for our $Cd_{0.92}Mg_{0.08}Te$ crystals, but within the band-tail states for as-grown crystals (see Fig. 1).

For the two-color experiments, the same 100-fs pulses were used, but in this case, the beam designated as the pump was frequency doubled using a BaB_2O_4 crystal to produce UV excitations well above the bandgap. The rest of the setup mirrored our one-color experiment, i.e., the probe signal was collected in the reflection mode. The two-color setup was used to study both CMgT:In and CMgT:Ge specimens. The pump power for these measurements was held fixed at 12 mW, while the probe power was 100 μW. In addition, for a series of CAP measurements, we used the two-color setup, but our Ti:sapphire laser was tuned from 750 nm up to 870 nm, in order to cover the widest possible range of probe wavelengths.

3.2. Femtosecond nonequilibrium carrier dynamics in (Cd,Mg)Te

For pump-probe measurements in the reflection mode, the experimental $\Delta R/R$ dependence can be expressed as [26]:

$$\Delta R/R = \frac{\Delta n}{n^2 - 1}, \tag{1}$$

where d is the film thickness and Δn is the photo-induced index of refraction change. For the probe photons with energies below the bandgap, Δn does not depend on the details of the electronic excitation spectrum and can be described by the Drude model, which relates it to the total free carrier concentration N [27]:

$$\Delta n = \frac{Ne^2}{2\epsilon_0 n_b m^* \omega^2}, \tag{2}$$

where e is the elementary charge, $n_b = \sqrt{\varepsilon_b/\varepsilon_0}$ is the background dielectric constant, m^* is the effective carrier mass and ω is the angular optical frequency.

Combing Eqs. (1) and (2), we see that in our experimental case, $\Delta R/R$ is simply proportional to $N(t)$. In the example trace shown in Fig. 3, the post-relaxation part of an experimental $\Delta R/R$ waveform can be very well represented by a phenomenological, double-exponential fitting:

$$\Delta R/R \propto \left[\exp\left(\frac{-t}{\tau_1}\right) + \exp\left(\frac{-t}{\tau_2}\right)\right], \tag{3}$$

with the initial fast relaxation time τ_1 ascribed, in our case, as the direct trapping of hot, highly-excited electrons, while the subsequent relatively much slow relaxation time τ_2 can be interpreted as the Shockley–Read–Hall recombination [28, 29].

Despite the perfect fit shown in Fig. 3, the physics insight in such a phenomenological approach is quite limited, so for a much more in-depth understanding of the carrier photo-excitation and, subsequent relaxation dynamics in our CMgT crystals, we have adopted a model presented in [30]. The model has been developed for nano-Si films, known to have extended concentration of trap states, and unifies the approaches presented in [31] and [32], for time-resolved carrier dynamics in amorphous Si films and in low-temperature-grown GaAs crystals, respectively. In our modeling, we include, besides the excitation, all scattering mechanisms of electrons that are reasonable for pump-probe characterization of our CMgT samples and then try to find the best fit to our $\Delta R/R$ experimental data.

Figure 4 shows schematically the CMgT energy diagram with in-gap trap states included, as well as carrier excitation and relaxation transitions (red and black arrows, respectively) in our one-color (800 nm–800 nm) pump-probe experiments. We can predict that carriers will be transferred near

the bottom of the conduction band via a direct band-to-band transition (process labeled $I\alpha$ in Fig. 4), or excited from the in-gap states that are expected to contain trapped electrons ($I\gamma$ in Fig. 4). In addition, especially for high intensity pump beams, we need to include a two-photon absorption (TPA) process ($I^2\beta$ in Fig. 4) that will create highly energetic, hot electrons. During the relaxation process, hot electrons can cool down by losing their energy through electron–optic-phonon interactions, τ_{cool}, gradually dropping towards the bottom of the conduction band, or be directly trapped by in-gap states, τ_{trap}. Simultaneously, electrons near the bottom of the conduction band can either be trapped (τ_{trap}) or non-radiatively recombine with holes, τ_{rec}. Finally, electrons released from traps can also recombine with holes with assumed, the same recombination time constant, τ_{rec}. For completeness, we have also included a possible, electron re-excitation process based on the optic-phonon-electron interaction with the time constant τ_{cool}.

Mathematically, the time dynamics of the carrier excitation/relaxation processes schematically presented in Fig. 4 can be described by the following three differential equations, presenting time evolutions of the concentrations of electrons near the bottom of the conduction band $N_{con}(t)$, highly-photoexcited, hot electrons $N_{hot}(t)$, and trapped electrons N_{trap}:

$$\frac{dN_{hot}}{dt} = \left(\frac{I}{h\nu}\right)^2 \beta + \frac{I\gamma}{h\nu} - \frac{N_{hot}}{\tau_{cool}} - \frac{N_{hot}}{\tau_{trap}} + \frac{N_c}{\tau_{cool}}, \tag{4}$$

$$\frac{dN_{con}}{dt} = \frac{I\alpha}{h\nu} - \frac{N_{con}}{\tau_{trap}} - \frac{N_{con}}{\tau_{cool}} - \frac{N_{con}}{\tau_{rec}} + \frac{N_{hot}}{\tau_{cool}}, \tag{5}$$

$$\frac{dN_{trap}}{dt} = -\frac{I\gamma}{h\nu} + \frac{N_{con}}{\tau_{trap}} + \frac{N_{hot}}{\tau_{trap}} - \frac{N_{trap} - N_{trap,final}}{\tau_{rec}}, \tag{6}$$

where I is the pump beam intensity, given as a Gaussian optical pulse $I(t) = I_o \exp\left(-4ln\left[2\,\frac{t^2}{\tau_p{}^2}\right]\right)$ with $\tau_p = 100$ fs (the width of our excitation pulse), $h\nu$ is the pump photon energy, α is the band-to-band absorption coefficient, τ_{cool} is the time constant for the electron–optic-phonon and optic-phonon–electron interactions, τ_{trap} is the time constant of the electron trapping process, τ_{rec} is the electron-hole recombination time, β is the TPA coefficient, γ is the trap-to-conduction band pumping coefficient, and, finally, $N_{trap,final}$ is the trap concentration at steady state. For high-intensity excitations it is reasonable to assume that there are more carriers than traps, and so, when the number of trapped electrons increases, fewer traps are available thus taking a longer time for electrons to "find" a place for trapping. Therefore, we assume that τ_{trap} is, as in [31], a function of the number of available trap sites and their individual lifetimes, and is given by:

$$\tau_{trap} = \frac{\tau_{trap,min}}{1 - \frac{N_{trap}}{N_{trap,max}}}, \tag{7}$$

with $N_{trap,max}$ and $\tau_{trap,min}$ representing the maximum concentration of trap sites in the sample and shortest trapping time, respectively.

Following Eqs. (1) and (2), our experimentally measured $\Delta R/R$ signal is directly proportional to the total carrier concentration $N(t)$. Thus, N(t) can be derived as:

$$N(t) = N_{hot}(t) + N_{con}(t) - N_{trap}(t), \quad (8)$$

where $N_{hot}(t)$, $N_{con}(t)$ and $N_{trap}(t)$ are the solutions of our starting differential Eqs. (4)-(6) Note that the sign in front of N_{trap} is negative, since traps reduce the concentration of excited free carriers.

3.3. Pump-probe experimental results and discussion

In order to understand the physics of the nonequilibrium relaxation dynamics of photo-excited carriers in our CMgT crystals (see Fig. 3 as an example), we fitted our experimentally measured probe $\Delta R/R$ waveforms to the trapping model [Eqs. (4)-(7)] presented in Sec. 3.2. Figures 5, 6, and 7 present typical $\Delta R/R$ waveforms (red dots) and the corresponding normalized $N(t)$ [eq. (8)] best fits (solid black lines). The inset in each figure shows the time evolutions of $N_{hot}(t)$, $N_{con}(t)$ and $N_{trap}(t)$, contributing to $N(t)$ for a given. Finally, the fitting parameters corresponding to each figure are listed in Tables 1, 2, and 3, respectively. We note that in each figure, numerical $N(t)$ dependences fit perfectly the experimental $\Delta R/R$ transients, as it is expected based on Eqs. (1) and (2). Therefore, the simulated $N_{con}(t)$, N_{hot}(t) and $N_{trap}(t)$ dependences, as well as the fitting parameters, present a detailed description of the physical processes governing both the carrier excitation and, subsequent, relaxation dynamics in our as-grown and annealed CMgT:In and CMgT:Ge samples.

One-color (800 nm–800 nm) pump-probe spectroscopy experiments were performed for CMgT:In as-grown and annealed samples and experimental waveforms as well as the fits are presented in Figs. 5(a) and 5(b) and Table 1, respectively. For the as-grown CMgT:In crystal [Fig. 5(a)], we note (Table 1) the extremely low ratio of $I^2\beta$, which refers to a negligible TPA process for the intensity of our pump beam used in the experiment. On the other hand, the value of $I\gamma$ is large and, actually, slightly larger than $I\alpha$. The latter means that trap pumping plays the most important role in our as-grown sample, since it is stronger than the conventional valence-to-conduction band transitions. The latter is clearly visible as an initial negative dip in the $N_{trap}(t)$ dependence, presented by the inset in Fig. 5(a). It indicates that part of free carriers is being trapped even during the excitation process and never directly reaches the conduction band. The inset in Fig. 5(a) also shows that $N_{trap}(t)$ represents the dominant contribution to $N(t)$, what, combined with the ultrashort value of τ_{trap}, much shorter than τ_{cool}, points out that there must be a very large number of traps in our as-grown sample. Actually, electron-phonon cooling process is, essentially, negligible (ultra large τ_{cool}), since there are, practically, no very hot electrons in our system, as the TPA process is

negligible. This is understandable because electron-phonon scattering is most relevant at the early stage of electron relaxation, when the carriers are exited highly into the conduction band by the intense pump beam. Finally, the carrier recombination time is ~5 ps, which means that the electron lifetime is short, as expected for a sample with very a large concentration of trap states.

We repeated the same one-color, pump-probe spectroscopy studies for an annealed CMgT:In sample and the experimental result, as well as the best fits, are shown in Fig. 5(b) and listed in Table 1. First we note that annealing significantly improved the transport properties of the sample. Looking at Table 1, we immediately note that, in contrast to the as-grown sample, the most dominant term now is the $I^2\beta$ TPA process, while the contribution from $I\alpha$ is negligible. The latter is the result that, as we have observed earlier, annealing practically removed the band-tail states at 1.55 eV energy (see Fig. 1), so our 800-nm pump photons do not have enough energy for the direct, across bandgap photo-excitation. We also notice a low value of the $I\gamma$ process indicating that traps are now less important due to their, apparently, diminished presence after the annealing process. Looking at time evolutions of our contributing densities presented by the inset in Fig. 5(b), we see that in the annealed sample, at the initial stage of relaxation the $N_{hot}(t)$ process is the dominant one and the τ_{cool} time is reduced, although not as much, as we would be expected based on the magnitude of $I^2\beta$. The later is, apparently, related to the fact that he negative dip in the $N_{trap}(t)$ dependence is still present albeit decreased, as compared to the as-grown case [see inset in Fig. 5(a)]. At longer times; however, traps still dominate and the carrier recombination time, although increased by the factor of 10, is still relatively short.

We have also performed two-color (400 nm–800 nm), pump-probe measurements for CMgT:In and CMgT:Ge specimens, both as-grown and annealed, respectively, and applied the fitting procedure. Since in this case, we used 400-nm-wavelength light for carrier pumping, we slightly modified our model by setting the TPA coefficient β to zero and replaced it with the term I_{uv} that excites carriers into the hot electron state, because our UV pump photons have an energy much larger than the material's bandgap. Experimental results and the best fits for CMgT:In as-grown and annealed samples are shown in Figs. 6(a) and 6(b), respectively, while the corresponding fitting parameters are listed in Table 2. As it can be observed in Table 2, the UV absorption is now the preferred pathway for free carrier excitation in both samples, while, the rate of trap pumping $I\gamma$ is negligible for the annealed one. The later case is, in fact, similar to the one-color measurement of an annealed CMgT:In sample; however, now we observe very effective relaxation of excited carriers by electron-phonon scattering, resulting in a much shorter τ_{cool} time. Furthermore, the model is able to identify a significantly increased relaxation time, τ_{rec}, in the annealed sample. The time evolution of the density of trap state carriers in the two-color measurement behaves similarly to the one-color case and it is a dominating factor for the as-grown sample. On the other hand, the $N_{hot}(t)$ process is the dominant one for the annealed sample. We also note that while the $\Delta R/R$ waveform [equivalently $N(t)$ dependence] for the as-grown sample exhibits a very large dip in the relaxation part of the curve, this dip is significantly reduced by annealing, indicating again that the annealing process visibly reduces the concentration of traps in the sample.

Figure 7 presents experimental results and model simulations for two-color measurements performed on CMgT:Ge as-grown [Fig. 7(a)] and annealed [Fig. 7(b)] specimens. The fitting parameters are listed in Table 3. As in the case of the CMgT:In sample, across the gap excitation I_{uv} is the preferred pathway for generating nonequilibrium carriers in both the as-grown and annealed samples, and the rate $I\gamma$ is again negligible for the annealed sample. However, the τ_{rec} time for the CMgT:Ge annealed sample is almost an order of magnitude shorter, as compared to $\tau_{rec} \approx 73$ ps for the annealed CMgT:In. The latter is due to the nature of the Ge dopant, which introduces deep states into the material's bandgap [21] and indicates that in this case, annealing is less effective at reducing Shockley-Read Hall recombination rate ($1/\tau_{rec}$), as compared to the In-doped samples. It is important, however, to notice that the magnitude of the negative dip in the $\Delta R/R$ data is greater for the un-annealed sample (Fig. 7a). Thus, the reduction in trap states for the Ge-doped sample improves the optical properties of the material, but not the electronic. Finally, the width of the initial photoresponse peak is roughly two times larger for the CMgT:Ge material, as compared to the CMgT:In one.

3.4. Coherent Acoustic Phonon detection and studies

During the course of our two-color pump-probe studies performed on both CMgT:In and CMgT:Ge samples, we consistently observed, weak, but very regular oscillations present on the relaxation part of $\Delta R/R$ waveforms (see insets in Fig. 8 for an annealed CMgT:In sample), when traced in the time delay range on the order of a nanosecond. These oscillations, not visible in Figs. 6 and 7 due to the short time windows, can be satisfactorily interpreted within the propagating strain-pulse model, introduced by Thomsen *et al*. [33] and Wu *et al*. [34]. The high energy and intense femtosecond pump pulse absorbed at the crystal surface introduces electronic as well as thermal stress [b] and generates a strain transient (lattice discontinuity) that propagates with a velocity of sound v_s into the sample at the direction orthogonal to the surface, locally altering its optical properties, namely, the refractive index of the crystal. The time-delayed probe beam penetrating the crystal is partially reflected from this travelling discontinuity and interferes with the part of the probe light reflected from the crystal surface resulting in the regular oscillations observed on top of the $\Delta R/R$ photoresponse signal and is interpreted as CAPs.

We stress that the strain transient consists of a very large superposition of individual CAP modes and the probe beam interference acts as "filter" for a given CAP mode, since it follows the momentum selection rule $q = k_i + k_f \approx 2nk_0$ where q is the wave vector of a given CAP mode, k_i and k_f are the initial and final wave vectors of the probe beam, n is the real part of the material's refractive index and k_0 is the probe beam wave vector in air [35]. Thus, probe photons of a given wavelength (equivalently k_0) scatter on the single CAP mode out of the strain transient.

[b]Electronic stress is the dominating factor; see [34].

The reflectivity change contribution to the probe self-interference and the frequency f of CAP oscillations are given by [33, 34]:

$$\Delta R(t) \propto \cos(2\pi f t - \varphi)\, e^{-t/\tau_d}, \tag{9}$$

$$f = \frac{n(\lambda) v_s \cos\theta}{\pi} k_{probe}, \tag{10}$$

where φ is the phase shift and τ_d is the CAP signal experimental decay time, while θ is the angle of probe light incident on the studied crystal and $k_{probe} = k_0$. In Eq. (10), we assume that τ_d arises from two sources, namely, CAP intrinsic lifetime τ_{phonon} and the penetration depth ζ (attenuation) of the probe light propagating into the crystal. Both contributions are independent, so τ_d can be expressed as a simple superposition:

$$\frac{1}{\tau_d} = \frac{1}{\tau_{phonon}} + \frac{1}{\zeta / v_s}. \tag{11}$$

In further discussion, we focus on experimental results for an annealed CMgT:In, as they are fully representative of the data collected for all our CMgT samples in two-color pump-probe measurements. Figure 8 shows oscillatory components (dots) of the $\Delta R/R$ transients obtained by subtracting the early-time, electronic component shown in Fig. 6(b) (main panel) from the full, long-delay–time (~500 ns) $\Delta R/R$ dependences presented in insets in Fig. 8. Figure 8(a) corresponds to the case when the wavelength of the probe beam was equal to 750 nm, i.e., probe photons have the energy above E_G, resulting in a substantial attenuation of the probe light as it propagates in the crystal, while in Fig. 8(b) the $\Delta R/R$ signal was collected for 800-nm probe light, what corresponds to the photon energy well below above E_G, where only a very minimal probe signal absorption is expected. The solid lines in Figs. 8(a) and 8(b) represent the fits obtained using Eq. (10). We note that as expected, in case of the above bandgap probing, the oscillatory signal in Fig. 8(a) is rather strongly attenuated with τ_d = 460.8 ps. This contrasts to Fig. 8(b), which shows no apparent sign of damping the oscillatory signal within the ~500 ps window, which led us to estimate τ_d in this case to be on the order of 10 ns, representing an upper limit on τ_{phonon}.

The CAP oscillations were collected for a full family of probe wavelengths (within the range from 750 nm up to 870 nm), fitted to Eq. 9, and in each case the oscillation frequency was extracted. Red circles in Fig. 9 represent the raw data as a function of the probe-light photon energy (top x-axis), or, equivalently, the wave number (bottom x-axis), for all tested wavelengths. Since the bulk of our collected CAP frequencies corresponds to probe wavelengths (photon energies) that are near/below the material's E_G, we needed to take into account in Eq. 10 the $n(\lambda)$ dependence to correct the raw data, using the $n(\lambda)$ measured with an ellipsometer (Fig. 2). Once the anomalous dispersion was factored in, the CAP frequency data (blue circles in Fig. 9) followed very accurately

the dispersionless, linear $f \propto k_{probe}$ relationship (see Eq. 10), as it is indicated by a crossing the original solid blue line fit in Fig. 9 The slope of the blue line corresponds to v_s, and was calculated to be 3367 m/s which agrees nicely with acoustic wave measurements involving the same material with (111) orientation [36].

As mentioned in connection with Eq. 11, for probe beam energies below E_G, the CAP signal attenuation τ_d is mainly due to the penetration depth of the probe beam and can expressed as $\tau_d \propto 1/v_s$ (see Eq. 11), since we know from the above E_G probe energy CAP measurements that the intrinsic τ_{phonon} is very long [see Fig. 8(b)]. In Fig. 10, we present ζ on the photon energy. Blue dots represent the annealed CMgT:In sample and the blue dashed line is just the guide to the eye. We can compare this dependence with the one expected for pure bandgap, direct semiconductors (black solid line), where $\zeta \propto (E^2-E_G^2)^{-1/2}$ E is the probe beam photon energy. We note that presence of sub-bandgap states results in a rather gradual increase of ζ (dashed line in Fig. 10), extending well into sub-band gap energies with the upturn starting near 1.56 eV. The latter is contrary to a very sharp increase of ζ at 1.62 eV predicted for a "clean" crystal (solid black curve in Fig. 10). The latter agrees very well with observations in [15] and [37], and confirms that extended band-tail states are the result of impurities, dopants or defects. For comparison, we also presented in Fig. 10 the $\zeta(E)$ dependence for an as-grown CMgT:In sample (red dots). In this case, we note that ζ is short in the entire tested range of probe beam energies with no clear upturn even at 1.55 eV, as in this sample-type sub-gap states are very extended [see Fig. 1(a)].

Conclusion

With the help of femtosecond pump-probe spectroscopy we were able to resolve the differences between the post-growth annealing processes for both sets of CMgT:In and CMgT:Ge samples. While the magnitude of the negative dip in our $\Delta R/R$ transients stood out as a key trait, our rate-equation model provided deep, physical insight into nonequilibrium carrier photo-excitation and, subsequent, relaxation following a number of scattering mechanisms involved. Based on the results from our modeling we discovered that the carrier relaxation rates were strongly affected by the concentration of traps present in our samples that, in turn were dependent on the annealing process. From the analysis relaxation processes, we concluded that the impact of annealing was most beneficial in the case of the In-doped CMgT sample. The latter leads us to the conclusion that the annealed CMgT:In single crystals are expected to be the better performing radiation detectors. Two-color studies enabled us to observe propagation of long-lived CAP modes excited by the pump photons. CAP propagation was dispersionless with the constant propagation velocity corresponding to the speed of sound in our CMgT. The intrinsic lifetime of CAPs was estimated to be as long as ~10 ns.

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Figure Captions

Figure 1: Tauc plots featuring absorption spectra versus photon energy (wavelength–top x axis) for (a) as-grown and annealed CMgT:In samples and (b) as-grown and annealed CMgT:Ge samples–red lines and blue lines, respectively. Linear extensions (dashed lines) crossing the x-intercept indicate the E_G values for each crystal.

Figure 2: Ellipsometry $n(\lambda)$ measurements of CMgT:In as-grown and annealed crystals. Experimental data (dots) are fitted to the nonlinear Schubert model for probe energies below the material E_G [23].

Figure 3: Normalized reflectivity transient change $\Delta R/R$ (black dots) measured in a one-color, pump-probe spectroscopy setup for an as-grown CMgT:In sample. The solid red line is the best fit to a bi-exponential decay function and the corresponding fitting parameters (see Eq. 3) are listed as the inset.

Figure 4: Schematic band diagram featuring our trapping model from Eqs. (4)-(6). The pumping scheme is applicable for a one-color pump-probe experiment.

Figure 5: Experimental data (red dots) from single-color pump probe measurements perfromed on (a) as-grown and (b) annealed CMgT:In samples. Simulation results from Eqs. (4)-(7) (inset) show the contributed carrier densities as a function of time. The superposition of all three contributing processes [see Eq. (7)], $N(t)$ is overlayed on the experimental data in the main panel (black line).

Figure 6: Experimental data (red dots) from two-color pump probe measurements perfromed on (a) as-grown and (b) annealed CMgT:In samples. Simulation results from Eqs. (4)-(7) (inset) show the contributed carrier densities as a function of time. The superposition of all three processes [see Eq. (7)], $N(t)$ is overlayed on the experimental data in the main panel (black line).

Figure 7: Experimental data (red dots) from two-color pump probe measurements perfromed on (a) as-grown and (b) annealed CMgT:Ge samples. Simulation results from Eqs. (4)-(7) (inset) show the contributed carrier densities as a function of time. The superposition of all three processes [see Eq. (7)], $N(t)$ is overlayed on the experimental data in the main panel (black line).

Figure 8: Experimental oscillations (dots) extracted from the full $\Delta R/R$ waveforms (insets) for an annealed CMgT:In sample, measured using a two-color pump-probe setup for (a) $\lambda_{probe} = 750$ nm (above E_G) and $\lambda_{pump} = 375$ nm, and (b) $\lambda_{probe} = 800$ nm (below E_G) and $\lambda_{pump} = 400$ nm. The blue, solid-line fits correspond to simple, damped sinusoidal oscillations [Eq. (9)].

Figure 9: Experimental CAP oscillation frequency dependence on the probe beam wavenumber/photon energy for an annealed CMgT:In sample. Red dots are raw experimental data, while blue dots are corrected for the anomalous dispersion $n(\lambda)$ dependence. The corrected data are fitted to the dispersionless relation, Eq. (10)–solid blue line passing through the origin

Figure 10: Penetration depth of the probe light vs. its energy obtained from the experimental decay time of CAP oscillations for annealed (blue dots) and as-grown (red dots) CMgT:In samples. For the annealed sample the solid black line presents the expected onset of increased penetration for a clean, direct-bandgap sample occurring at 1.62 eV, while the dashed line (the guide to the eye) indicates the actual onset of increased penetration in our sample, suppressed due to the presence of sub-bandgap states.

Tables

Table 1: Fitting parameters for as-grown and annealed CMgT:In samples measured using a one-color (800-nm wavelength) pump-probe setup with 36-mW pump and 3-mW probe beams. All of the fitting parameters are based on Eqs. (3)-(6).

	$I\alpha$	$I^2\beta$	$I\gamma$	τ_{trap} (ps)	τ_{cool} (ps)	τ_{rec} (ps)
As grown	4.04 ± 0.9	0.001 ± 0.00001	5.19 ±0.32	0.15 ± 0.001	5828 ± 15.9	4.76 ±0.76
Annealed	0.012 ± 0.000001	9.08 ± 0.01	0.56 ± 0.05	0.67 ± 0.12	4441 ± 1.89	43.16 ± 1.3

Table 2: Fitting parameters for as-grown and annealed CMgT:In samples measured using a two-color (400-nm/800-nm) pump-probe setup with 12-mW pump and 100-μW probe beams. All of the fitting parameters are based on Eqs. (3)-(6).

	I_{uV}	$I\gamma$	τ_{trap} (ps)	τ_{cool} (ps)	τ_{rec} (ps)
As grown	2.32 ± 0.12	0.97 ± 0.03	0.52 ± 0.09	1.58 ± 0.4	3.57 ± 0.63
Annealed	4.08 ± 0.22	0.00063 ±0.00004	0.52 ± 0.18	1.78 ± 0.5	73.1 ± 9.3

Table 3: Fitting parameters for as-grown and annealed CMgT:Ge samples measured using a two-color (400-nm/800-nm) pump-probe setup with 12-mW pump and 100-μW probe beams. All of the fitting parameters are based on Eqs. (3)-(6).

	I_{uv}	$I\gamma$	τ_{trap} (ps)	τ_{cool} (ps)	τ_{rec} (ps)
As-grown	1.65 ± 0.25	1.13 ± 0.6	0.52 ± 0.11	1.65 ± 0.19	2.7 ± 0.8
Annealed	4.02 ± 0.52	0.01 ± 0.005	0.52 ± 0.23	1 ± 0.49	10.79 ± 2.7