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We report on the nonlinear optical properties of few-layer GaTe studied by multiphoton microscopy. Second and third harmonic generation from few-layer GaTe flakes were observed in this study with the laser pump wavelength of 1560 nm. These processes were found to be sensitive to the number of GaTe layers. The second- and third-order nonlinear susceptibilities of 2.7 × 10^{-19} esu (1.15 pm/V) and 1.4 × 10^{-8} esu (2 × 10^{-16} m²/V²) were estimated, respectively. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4941998]

Semiconducting 2D materials are attracting considerable interest for research aimed at applications in next-generation electronics and optoelectronics. Many layered 2D materials with a broad range of properties have been explored, from insulating h-BN and semi-metallic graphene to semiconducting layered metal chalcogenides (e.g., MoS₂, WS₂, GaSe, GaS). Optical properties of graphene have been exploited in various photonic devices. Recently, monolayer MoS₂ has garnered significant interest in nonlinear optics as the lack of inversion symmetry yields a non-vanishing second-order susceptibility. Strong second-harmonic generation (SHG) and third-harmonic generation (THG) have also been reported for few-layer GaSe.

Similar to GaSe, GaTe is a non-centrosymmetric 2D layered material having an anisotropic monoclinic crystal structure with each layer consisting of Te-Ga-Ga-Te repeat units stacked along the c-axis. Bulk GaTe has strong excitonic absorption at room temperature and also exhibits high carrier mobilities and long carrier lifetimes showing excellent electronic and optical properties and therefore has been applied in optoelectronic devices, radiation detectors, and solar cells.

In contrast to these studies, very little is known about the nonlinear optical properties of few-layer GaTe although they can play an important role in various photonic and optoelectronics applications. Nonlinear absorption properties for wavelengths shorter than 1064 nm have been reported for bulk GaTe crystals. In order to have SHG, it is essential to have material with broken inversion symmetry. GaTe exhibits such broken inversion symmetry regardless of the number of layers, N. This is an exceptional characteristic compared to MoS₂, where SHG can only be observed in the case of monolayer and odd N as the inversion symmetry is broken only in these cases. Even with odd N, the SHG signal of MoS₂ is significantly reduced with increasing N. The broken inversion symmetry that persists in GaTe regardless of N inspires the careful study of few-layer samples. This is a critical aspect from a material manufacturing standpoint as well, since controlling the uniformity and number of layers has been extremely challenging in chemical vapour deposition (CVD) of 2D materials other than graphene.

In this work, we have employed multiphoton microscopy with a compact 1560 nm femtosecond fiber laser to study the nonlinear optical properties of GaTe, specifically second and third harmonic generation in mechanically exfoliated few-layer GaTe. Employing multiphoton microscopy, we obtain high-contrast signals for different layer thicknesses of GaTe and the substrate. A systematic optical nonlinearity study focusing on THG and SHG of few-layer GaTe is carried out using the laser excitation wavelength near 1560 nm, in a technologically important telecommunication window, where applications of second- and third-order nonlinearities, e.g., all-optical signal processing and frequency conversion, may have ground-breaking impact. A confocal scanning micro-Raman system with a 532 nm green laser was used for Raman studies at room temperature in ambient air. Figure 1(a) shows an optical image displaying different thicknesses of exfoliated GaTe flakes as determined by atomic force microscopy (AFM) in Figure 1(b). The thickness of single-layer GaTe is known to be ∼0.75 nm. Raman mapping of the flake (integrated intensity in the range of 152–212 cm⁻¹) is presented in Figure 1(c). Three prominent peaks can be observed in the Raman spectra in Figure 1(d) at 178 cm⁻¹, 233 cm⁻¹, and 275 cm⁻¹. Note that the system employed is not able to detect Raman shifts below 150 cm⁻¹.

The Raman peak around 178 cm⁻¹ is clearly visible for thicknesses from 7 nm to 17 nm (Figure 1(d)). At around 57 nm thickness, the peak has the same spectral characteristics as can be noted in Figure 1(e) although the signal intensity is in overall quite low. We assume that the reduced intensity relates to light absorption in GaTe, which reduces the...
The Raman peak around the 275 cm$^{-1}$ is quite strong from areas having a thickness of 14–17 nm, whereas it is undetectable for thinner areas (7–11 nm). A peak at 233 cm$^{-1}$ is observed from 11 to 17 nm thick flakes with an intensity that increases with thickness, whereas at ~57 nm the peak intensity becomes very low. An additional peak with relatively low intensity appears at 223 cm$^{-1}$ when the thickness reaches ~57 nm. It should be noted that the Raman peak around 307 cm$^{-1}$ originates from the substrate and can also be seen in the spectra from the thin GaTe layers as evidenced in Figure 1(e). Furthermore, this peak is practically absent for the thicker layer as expected due to signal absorption in GaTe.

To study the nonlinear optical properties of few-layer GaTe, we employed a multiphoton microscope with a compact 1560-nm femtosecond fiber laser. Details of the system can be found in Ref. 22. SHG and THG images taken simultaneously using a dichroic mirror in the multiphoton microscope are shown in Figures 2(a) and 2(b), respectively. The areas with different number of layers are clearly distinguishable in the THG image. Both SHG and THG signal intensity increase as the number of layers increases. For further visualization, Figure 2(c) shows a composite RGB (Red Green Blue) micrograph obtained by combining images in Figures 2(a) and 2(b). The SHG and THG signals are in the red and green channels of the RGB image, respectively. The areas in Figure 2(c) that simultaneously show a high intensity for both SHG and THG signals appear in the composite image as yellow (combination of red and green). The cross-sectional profiles of the SHG and THG signals from the blue dashed line in Figure 2(c) are plotted in Figure 2(d). Interestingly, the maximum intensity of SHG and THG is not observed to arise from the thickest (57 nm) area of the flake. Instead, a clearly distinct high intensity region can be discriminated in the region between the 17-nm-thick and 57-nm-thick areas for both signals. The AFM micrograph of this area in Figure 2(e) reveals that there is a staircase-like structure. From the AFM cross-section plotted in Figure 2(f), we estimate that the step height is about 10 nm for each step. In the case of the 57-nm-thick area, we attribute the decreased SHG and THG signals to the increased flake thickness compared to the coherence length (as discussed below).
The THG image shows higher contrast between the substrate and GaTe. This holds true also when assessing the contrast between different numbers of layers in the flake. For our setup, the THG signal from the 7-nm-thick flake is relatively weak (becoming nearly indistinguishable). For the SHG signal, the corresponding threshold thickness seems to be 11 nm. The weak signals are probably due to the small thickness of the flake compared to the coherence length of the materials (as we consider later in detail). THG signals are constant over areas with the same $N$, whereas the SHG signals seem to vary even within areas of constant $N$, perhaps indicating variations in the crystal structure or the presence of stresses, which could affect the second order nonlinear optical susceptibility.

To further analyse the nonlinear optical effects, the SHG and THG signals for different layer thickness are plotted versus the excitation peak power in Figures 3(a) and 3(b). The SHG and THG signals follow square and cubic behaviour, respectively, as expected. This underscores that the observed signals originated from SHG and THG. Both measurements confirm that the maximum signal intensity is achieved for GaTe when the thickness is below 57 nm.

The coherence length for the backward generated THG can be calculated from $\beta_{THG} \approx \frac{1}{k_{THG}(\omega)+3k_{(2\omega)}} \approx \frac{1}{6(n_{\omega}+n_{3\omega})}$. With the excitation wavelength $\lambda = 1560$ nm, we use the effective indices of $n_{\omega} = 3.8$ (at the wavelength of 1560 nm) and $n_{3\omega} = 3.76$ (at the wavelength of 518 nm) for fundamental and THG signal, respectively.\textsuperscript{14} $n_{3\omega} < n_{\omega}$ (i.e., anomalous dispersion) due to the position of the band gap in GaTe, which lies in between the two wavelengths. The calculated $\beta_{THG}$ is about $34 \text{ nm}$. For SHG, $\beta_{SHG} \approx \frac{1}{4(n_{2\omega}+n_{\omega})} \approx 46 \text{ nm}$ using $n_{2\omega} \approx 4.72$ (from Refs. \textsuperscript{14} and \textsuperscript{23} for the wavelength of 776 nm, just below the band gap). For both SHG and THG, the coherence length (for the backward generated SHG and THG) lies between 17 and 57 nm. Below the coherence length, the harmonic signals should increase when the thickness of the non-linear material increases, and above the coherence length the signal starts to decrease. This is why we observed the highest SHG and THG signals from the staircase area shown in Figure 2(e), with thickness between 17 and 57 nm.

The spectra of the generated light were measured at two different positions with different thickness (11 nm and 57 nm). Figure 4 shows peaks at the wavelength of 520 nm and 780 nm observed in both measurements. The positions and narrowness of the peaks further verify that the detected signals are second and third harmonics for the fundamental excitation wavelength of 1560 nm as opposed to multiphoton fluorescence. In the area with a thickness of 11 nm, the peak near 780 nm is not as intense as in the area having a thickness of 57 nm. The weak signal from 11 nm thick GaTe is probably due to the small thickness compared to the coherence length or could indicate some modification in the structure for thicker films.

The third-order optical nonlinearity coefficient $\chi_{GaTe}^{(3)}$, was estimated to be around $1.382 \times 10^{-7}$ esu ($2 \times 10^{-16}$ m$^3$/V$^2$) using single-layer graphene as a reference ($\chi_{graphene}^{(3)} \approx 3 \times 10^{-7}$ esu).\textsuperscript{21} The estimation was performed with the following relationship:\textsuperscript{12}

$$\chi_{GaTe}^{(3)} \approx \frac{d_{graphene}}{d_{GaTe}} \sqrt{\frac{THG_{GaTe}}{THG_{graphene}}} \chi_{graphene}^{(3)},$$

where the thickness of graphene $d_{graphene}$ is 0.3 nm, $d_{GaTe}$ is 11 nm, and

$$THG_{GaTe}/THG_{graphene} = 2.79.$$
laser power of the SHG signal on the 14nm thick GaTe flake $P_{av2} = 8.93 \times 10^{-13}$ W, numerical aperture NA = 0.5, permittivity of free space $\varepsilon_0 = 8.854 \times 10^{-12}$ Fm$^{-1}$, velocity of light $c = 2.99 \times 10^8$ m$^{-1}$s, and the wavelength of the SHG signal $\lambda_2 = 780$nm were used to calculate the sheet nonlinear susceptibility of 14-nm-thick GaTe. The calculated sheet nonlinear susceptibility is $6.72 \times 10^{-22}$ m$^2$/V. Taking the thickness into account, the estimated second-order nonlinear susceptibility of the material is about 1.15pm/V ($2.7 \times 10^{-15}$ esu).

For comparison to other layered 2D materials, $\chi^{(2)} = 20 \pm 2$ pm/V has been reported for the few layer GaSe at the excitation wavelength of 1560 nm. The $\chi^{(2)}$ literature values for monolayer MoS$_2$ are on the order of hundreds of pm/V (Refs. 11 and 27) at excitation wavelengths around 800 nm. $\chi^{(2)} = 4.5$ nm/V has been reported for synthesized monolayer WS$_2$ at an excitation wavelength of 832 nm. Therefore, we conclude that the second-order nonlinearity coefficient of GaTe is around two and three orders of magnitude lower than the $\chi^{(2)}$ of MoS$_2$ and WS$_2$ measured at the wavelength of ~800 nm, respectively. However, our measurements have been done at the wavelength of 1560 nm, and therefore, the second-harmonic wavelength is 780 nm (lower photon energy than the band-gap). This surely affects the magnitude of the second-order nonlinearity. Our recent study on the optical nonlinearities in exfoliated monolayer MoS$_2$ estimates that $\chi^{(2)}$ is around 2.2 pm/V at the excitation wavelength of 1560 nm, which is comparable to that of GaTe in this work. While this $\chi^{(2)}$ figure is lower than for, e.g., MoS$_2$ monolayer, GaTe has the advantage that its frequency conversion processes are enhanced directly with increasing $N$, unlike with MoS$_2$. It is evident that further studies are needed to establish a clear picture and consensus regarding the basic nonlinear optical material properties of the 2D materials beyond graphene. Our results indicate that GaTe is an interesting material among the layered 2D materials and deserves further study.

In conclusion, the optical nonlinearity of GaTe was investigated using multiphoton microscopy with an excitation wavelength of 1560 nm. A systematic optical nonlinearity study of few-layer GaTe is carried out. The SHG and THG signals showed clear contrast for different number of GaTe layers, and we observed that the SHG and THG signals increase monotonically with layer thickness until the coherence lengths of the material are reached. This shows that, unlike with, e.g., MoS$_2$, the nonlinear optical coefficients of GaTe do not decrease with increasing material thickness. We also determined the THG and SHG optical nonlinearity susceptibilities for GaTe. Nonlinear optical effects can be used for rapid characterization of atomically thin films of GaTe and other similar materials.

Sample preparation: GaTe flakes were grown by the Bridgman method. Few-layer flakes of GaTe were obtained by mechanical cleaving from a bulk single crystal. Utilizing adhesive tape, exfoliation was carried out in ambient air. Flakes were deposited on an oxidised silicon substrate with an oxide thickness of 285 nm. Few-layer GaTe flakes were identified using optical microscopy and the number of layers was determined by AFM.

Raman spectroscopy: A confocal scanning micro-Raman system with a 532 nm green laser was used to measure samples at room temperature in ambient air. The measurements were carried out within a few hours after mechanical cleaving to avoid any degradation of the sample. The spectra were averaged in the different regions. The spectral dependence of the Raman signal on layer thickness was observed. Controlled experimental procedures, such as avoiding exposure to high laser power, were employed to minimize possible degradation of GaTe.

Multiphoton microscopy: The nonlinear optical properties of the GaTe flakes were investigated using a unique, in-house built multiphoton microscope. The design of the microscope, and the experimental procedure have been reported previously. The light source in the system is an amplified erbium-doped mode-locked fiber laser operating at a central wavelength of 1560 nm. The maximum average power of the laser is 60 mW with a repetition rate of 75 MHz and 228 fs pulse duration at the sample surface. The pulse peak power is estimated to be 3.5 kW and pulse energy is 0.8 nJ. The laser beam is scanned with a 2D galvo mirror system and focused on the sample surface using a 20× microscope objective (New Focus, 5724-H-C, 0.5 NA); the measured focal spot size is 1.3 μm. The backscattered second- and third-harmonic signals generated from each point on the sample are split into two paths using a long-pass dichroic mirror (cut-off at 562 nm) and then detected using photomultiplier tubes (PMTs). Narrow band-pass filters are used to select SHG and THG signals at a central wavelength of 780 nm and 520 nm, respectively. The acquisition of the two channels is simultaneous, making the measurement conditions for both channels exactly identical regardless of any perturbations (such as external vibrations or fluctuations in laser power). The technique is very fast compared to conventional Raman mapping and well suited for characterization of samples with large surface area.

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