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Ultra-broadband enhanced nonlinear saturable absorption for Mo$_{0.53}$W$_{0.47}$Te$_2$ nanosheets

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Alloying in two-dimension has been a hot spot in the development of new, versatile systems of optics and electronics. Alloys have been demonstrated to be a fascinating strategy to modulate the chemical and electronic properties of two-dimensional nanosheets. We firstly reported ultra-broadband enhanced nonlinear saturable absorption of Mo$_{0.53}$W$_{0.47}$Te$_2$ alloy at 0.6, 1.0, and 2.0 μm. The nonlinear saturable absorption of Mo$_{0.53}$W$_{0.47}$Te$_2$ saturable absorber (SA) was measured by the open aperture Z-scan technique. Compared to MoTe$_2$ and WTe$_2$ SAs, the Mo$_{0.53}$W$_{0.47}$Te$_2$ SA showed five times deeper modulation depth, 8.6% lower saturable intensity, and one order larger figure of merit. Thus, our research provides a method of alloys to find novel materials with more outstanding properties for optics and optoelectronic applications.

Two-dimensional (2D) transition metal dichalcogenides (TMDs) have attracted considerable attention for nanoelectronic and optoelectronic applications because of their attractive carrier mobility, adjustable bandgap, light-matter interaction, and stable chemical properties. The similar structure of MX$_2$ (WS$_2$, WSe$_2$, WTe$_2$, MoS$_2$, MoTe$_2$, etc.) is that the transition metal (M) atoms are sandwiched between two layers of chalcogen atoms (X). TMDs are the molecular layers formed by strong intralayer chemical bonding and the weak van der Waals forces inter layer. The layered structure allows us to use top-down exfoliation to obtain mono- and few-layer nanoflakes by mechanical or chemical processes. The electronic properties of TMDs vary from semiconducting to metallic due to the precise elementary composition and geometry. The semiconductors of TMDs can potentially serve as saturable absorbers (SAs), such as molybdenum disulfide and tungsten disulfide SAs, which already exhibit promising applications with much deeper modulation depth than graphene, but only in the visible range. The semi-metallic property of TMDs such as WTe$_2$ extends the SA working band, but the modulation depth is relatively low due to its stronger reflection of excitation light. To obtain novel SAs with more outstanding properties is the goal of SAs research.

TMD alloys provide a reasonable approach to tailor their physical and chemical properties. Element doping in TMD alloys is a substitutional doping rather than dopants occupying interstitial and defect sites. The different phases and electronic structures of TMDs facilitate us to obtain adjustable, broadband, and optimized properties by alloying. Several ultra-thin ternary TMDs have been successfully prepared (e.g., MoS$_2$, Se$_{2(1−x)}$) and Mo$_x$W$_{1−x}$Te$_2$. However, only a few hundred milli-electron volts (meV) can be tuned, i.e., 80 meV for MoS$_2$, Se$_{2(1−x)}$ and 170 meV for Mo$_x$W$_{1−x}$Te$_2$ solid solutions, respectively. The WSe$_2$ with 2H phase shows the semiconductor properties, while the semiconducting (Td) WTe$_2$ shows a semimetallic property, displaying giant magnetoresistance. Yu et al. experimentally showed that WSe$_2$, Te$_2$, and 1Td structures for x = 0.5 and 0.4. On a similar note, a series of Mo$_x$W$_{1−x}$Te$_2$ single crystals by the chemical vapor transport (CVT) method were synthesized. The phase transition was obtained by controlling the chemical ratio of Mo$_x$W$_{1−x}$Te$_2$ gradually changing from the 2H phase (β) to the Td phase. Mo$_{0.53}$W$_{0.47}$Te$_2$ was identified as the mixture phases of β and Td, which was due to the residual phase in the process of phase transition. The β and Td mixture phases of Mo$_{0.53}$W$_{0.47}$Te$_2$ can introduce extraordinary physical properties needed for an-depth study. Compared to 2D binary TMDs, the alloys showed unique advantages making them fundamentally and technically important in applications of optics and optoelectronics. Surprisingly, excellent nonlinear optics (NLO) properties of mono- and few-layer alloys were studied by Wang et al., where Bi$_x$Te$_y$Se$_{3−x}$ alloys showed lower saturable intensity and deeper modulation depth.

Here, we firstly report the ultra-broadband and enhanced nonlinear SA of ternary Mo$_{0.53}$W$_{0.47}$Te$_2$. Based on the nonlinear optical theory model of Z scan, Mo$_{0.53}$W$_{0.47}$Te$_2$ SA showed five times deeper modulation depth, 8.6% lower saturable intensity, and one order larger figure of merit (FOM) than those of MoTe$_2$ and WTe$_2$ SAs. Thus, our research provides a method of alloys...
for finding novel materials with more outstanding properties for optics and optoelectronic applications.

We prepared Mo$_{0.53}$W$_{0.47}$Te$_2$ SAs by liquid-phase exfoliation and spin-coating technique in this work. For further comparison, the WTe$_2$ and 2H-MoTe$_2$ SAs were treated by the same parameters in liquid-phase exfoliation and spin-coating processes\cite{215}. Transmission electron microscopy (TEM) was employed to examine the morphology of the Mo$_{0.53}$W$_{0.47}$Te$_2$, 2H-MoTe$_2$, and WTe$_2$. As shown in Figs. 1(a)–1(c), the layered structures of Mo$_{0.53}$W$_{0.47}$Te$_2$, 2H-MoTe$_2$, and WTe$_2$ could be seen, indicating that liquid-phase exfoliation was an effective method to obtain nanosheets. The spots of selected area electron diffraction (SAED) in the inset of Figs. 1(a)–1(c) indicated monocrystalline features of Mo$_{0.53}$W$_{0.47}$Te$_2$, 2H-MoTe$_2$, and WTe$_2$ nanoflakes. To identify the elemental ratio of the synthesized alloy, energy dispersive spectroscopy (EDS) was utilized. As shown in Figs. 1(d)–1(f), the chemical characterizations conformed to the stoichiometric ratio in the synthesis step. It can be seen that the ratio of Mo and W in Mo$_{0.53}$W$_{0.47}$Te$_2$ was 0.53 to 0.47, indicating an efficient doping of W ions in the MoTe$_2$ framework. Furthermore, atomic force microscopy (AFM) was employed to measure the three SAs’ thicknesses, as shown in Figs. 1(g)–1(i). The heights of Mo$_{0.53}$W$_{0.47}$Te$_2$, 2H-MoTe$_2$, and WTe$_2$ nanoflakes were about 5.32, 5.62, and 5.65 nm, corresponding to the number of layers of 8, 9, and 9, respectively.

Raman spectroscopy was carried out to provide lattice vibration modes of synthesized Mo$_{0.53}$W$_{0.47}$Te$_2$. The study was carried out using a Jobin Yvon LabRam 1B Raman spectrometer with a laser at 532 nm. Figure 2 shows the Raman spectra of Mo$_{0.53}$W$_{0.47}$Te$_2$, MoTe$_2$, and WTe$_2$. The prominent peaks of the Mo$_{0.53}$W$_{0.47}$Te$_2$ alloy can be defined as A$_1$-like (211.5 cm$^{-1}$) and A$_5$-like (263.2 cm$^{-1}$) modes based on the dominant direction of phonon vibrations. The A$_1$-like mode of Mo$_{0.53}$W$_{0.47}$Te$_2$ resulted from the corresponding modes in WTe$_2$. The shift of 0.9 cm$^{-1}$ A$_1$-like mode was attributed to the significant changes in the electron–phonon coupling softened by the binary component MoTe$_2$. The frequency shift of 4.7 cm$^{-1}$ at the A$_5$-like mode of Mo$_{0.53}$W$_{0.47}$Te$_2$ originated from the extra strain due to the different atomic radius of W and Mo. The Mo$_{0.53}$W$_{0.47}$Te$_2$ showed multiple peaks of the $\beta$- and Td-phase, indicating that Mo$_{0.53}$W$_{0.47}$Te$_2$ was a mixture of phases $\beta$ and Td, which may be formed due to the residual phases after the phase transition. The reflectance spectrum of metallic Mo$_{0.53}$W$_{0.47}$Te$_2$ showed significantly enhanced light absorption over a wide range of wavelengths due to strong absorption of MoTe$_2$. Furthermore, Mo$_{0.53}$W$_{0.47}$Te$_2$ also had a relatively flat absorption curve with stronger absorption due to the combination of linear absorption of MoTe$_2$ and WTe$_2$. The 2H-MoTe$_2$ showed two absorption peaks located at the wavelengths of 403 nm and 762 nm, which coincided with spin-orbit splitting. Based on the Lorentz–Drude model, the fitted lines of transmittance were dashed lines shown in Fig. 2(b). The refractive indexes of the three SAs shown in Fig. 2(c) were calculated by the relationship of Kramers–Kronig\cite{16,18}.

We adopted the most popular open aperture Z-scan measurements to obtain the nonlinear optical response. Mode-locked lasers operating at 0.639, 1.060, and 2.0 $\mu$m with 80 MHz repetition rate and 175 fs pulse width were used to study the NLO behavior of the Mo$_{0.53}$W$_{0.47}$Te$_2$ SA. The NLO response of Mo$_{0.53}$W$_{0.47}$Te$_2$ nanosheets could be clearly seen in Fig. 3. The increase of transmittance was easily observed with the increase of laser intensity, resulting from the nonlinear saturable absorption effect.

Based on the theory of NLO, the total absorption $\alpha(I)$ consists of a linear absorption coefficient $\alpha_0$ and a nonlinear absorption coefficient $\alpha_{NL}$. The absorption coefficient $\alpha(I)$ is expressed as
Based on Beer–Lambert law, the propagation equation format is shown as
\[
\frac{dI}{dz} = -\alpha(I)I.
\] (2)

By fitting the Z-scan data with Eqs. (1) and (2), we can obtain the \(\alpha_{NL} \sim 10^4 \text{ cm/GW}\) of the Mo0.53W0.47Te2 and MoTe2 nanosheets. The imaginary part of the third-order NLO susceptibility \(\text{Im}^{(3)}\) and the FOM for the third-order NLO are represented as
\[
\text{Im}^{(3)}(\text{esu}) = \left(10^{-7} c \lambda n^2/96 \pi^3\right) \times \alpha_{NL} \left(\frac{\text{cm}}{\text{W}}\right),
\] (3)
\[
\text{FOM} = |\text{Im}^{(3)}/\alpha_0|,
\] (4)
where \(c\) is the speed of light, \(\lambda\) is the laser light wavelength, and \(n\) is the refractive index calculated by the relationship of Kramers–Kronig. Based on Eq. (1), we calculated the \(\text{Im}^{(3)}\) FOM in Table 1. Compared to graphene, graphene oxide, and MoS2/N-methyl-2-pyrrolidone (NMP) dispersions of \(\sim 10^{-15} \text{ cm} \cdot \text{esu}\), the FOM of Mo0.53W0.47Te2 was \(\sim 10^{-10} \text{ cm} \cdot \text{esu}\), five orders of magnitude larger\[\text{19}\]. The results showed the Mo0.53W0.47Te2 nanosheets exhibited excellent nonlinearity. Due to the value of FOM varied with the difference of SA thicknesses and the preparation processes, we carried out the Z scan on the same condition, and the three SAs were prepared by the same parameters of liquid-phase exfoliation and spin-coating technique. The FOM value of the Mo0.53 W0.47Te2 SA was larger than those of WTe2 and MoTe2 SAs, which indicated the enhanced nonlinear performance.

In another NLO theory model, transmittance of the Mo0.53W0.47Te2 nanosheets is expressed in the form of
\[
T = 1 - A_s \times \exp \left(-\frac{I}{I_{\text{sat}}} - A_{\text{nS}}\right),
\] (5)
where \(A_s\) is the modulation depth, \(A_{\text{nS}}\) is the non-saturable components, \(I_{\text{sat}}\) is the saturable intensity, and \(I\) is the incident light intensity. We fitted the Z-scan data with Eq. (5), and the modulation depth and saturable intensity were obtained, respectively. The results are illustrated in Table 1. It should be noted that compared to WSe2 and WTe2 SAs, saturation intensity and modulation depth of the Mo0.53 W0.47Te2 were lower and deeper at 0.639, 1.060, and 2.0 \(\mu\)m. Mo0.53 W0.47Te2 can reach the saturable station at intensities of 1.82, 1.12, and 2.8 GW/cm\(^2\) at the wavelengths of 0.639, 1.060, and 2.0 \(\mu\)m, respectively. Compared to the MoTe2 SA, the Mo0.53 W0.47Te2 SA

### Table 1. Optics Parameters of Mo0.53W0.47Te2, 2H-MoTe2, and WTe2

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\lambda) ((\mu)m)</th>
<th>(n)</th>
<th>(\alpha_0) (10(^4) cm(^{-1}))</th>
<th>(\alpha_{NL}) (10(^3) cm/GW)</th>
<th>(\text{Im}^{(3)}) (10(^{-6}) esu)</th>
<th>FOM (10(^{-10}) cm \cdot esu)</th>
<th>(I_s) (GW/cm(^2))</th>
<th>(A_s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo0.53 W0.47Te2</td>
<td>0.639</td>
<td>5.7</td>
<td>3.07</td>
<td>-42.10</td>
<td>-26.287</td>
<td>8.562</td>
<td>1.82</td>
<td>6.50%</td>
</tr>
<tr>
<td></td>
<td>1.06</td>
<td>5.9</td>
<td>3.05</td>
<td>-65.10</td>
<td>-72.313</td>
<td>23.787</td>
<td>1.12</td>
<td>5.40%</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>7.1</td>
<td>3.05</td>
<td>-52.10</td>
<td>-168.366</td>
<td>55.202</td>
<td>2.8</td>
<td>4.20%</td>
</tr>
<tr>
<td>MoTe2</td>
<td>0.639</td>
<td>2.7</td>
<td>1.06</td>
<td>-4.71</td>
<td>-0.682</td>
<td>0.226</td>
<td>8.7</td>
<td>5.89%</td>
</tr>
<tr>
<td></td>
<td>1.06</td>
<td>0.33</td>
<td>1.08</td>
<td>-4.01</td>
<td>-0.014</td>
<td>0.013</td>
<td>12.9</td>
<td>4.30%</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>0.11</td>
<td>0.92</td>
<td>-2.97</td>
<td>-0.002</td>
<td>0.003</td>
<td>4.24</td>
<td>1.17%</td>
</tr>
<tr>
<td>WTe2</td>
<td>0.639</td>
<td>11.7</td>
<td>0.82</td>
<td>-1.31</td>
<td>-3.40</td>
<td>4.13</td>
<td>3.04</td>
<td>1.30%</td>
</tr>
<tr>
<td></td>
<td>1.06</td>
<td>11.6</td>
<td>1.08</td>
<td>-1.50</td>
<td>-6.46</td>
<td>5.97</td>
<td>4.43</td>
<td>2.21%</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>11.6</td>
<td>0.92</td>
<td>-1.46</td>
<td>-12.50</td>
<td>13.58</td>
<td>13.9</td>
<td>1.87%</td>
</tr>
</tbody>
</table>

Fig. 3. Open-aperture Z-scan results of Mo0.53W0.47Te2, MoTe2, and WTe2 at (a) 639 nm, (b) 1060 nm, and (c) 2 \(\mu\)m.
exhibited 8.6% lower saturable intensity at 1 μm. Compared to the WTe$_2$ SA, the Mo$_{0.53}$W$_{0.47}$Te$_2$ SA exhibited five times deeper modulation depth at 0.639 μm. It was consistent with the stronger linear absorption, as shown in Fig. 2(b).

In conclusion, we firstly, to the best of our knowledge, report the ultra-broadband and enhanced nonlinear saturable absorption of ternary Mo$_{0.53}$W$_{0.47}$Te$_2$ with mixture phases of β and Td. The SAED, EDS, and Raman spectra showed that the alloy Mo$_{0.53}$W$_{0.47}$Te$_2$ nanosheets had good quality. The nonlinear saturable absorptions of the filmy Mo$_{0.53}$W$_{0.47}$Te$_2$ SA were also measured by the open aperture Z-scan technique. Mo$_{0.53}$W$_{0.47}$Te$_2$ SA showed five times deeper modulation depth compared to WTe$_2$ SA at 639 nm; the Mo$_{0.53}$W$_{0.47}$Te$_2$ SA showed 8.6% lower saturable intensity and three-orders larger FOM compared to the MoTe$_2$ SA at 1060 nm and 2 μm, respectively. Thus, our research provides a method to find novel materials with more outstanding properties for optics and optoelectronic applications.

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References