Optical limiting properties of Te and Ag$_2$Te nanowires

C.S. Suchand Sandeep [a], A.K. Samal [b], T. Pradeep [b,*], Reji Philip [a,*]

[a] Raman Research Institute, C.V. Raman Avenue, Sadashivanagar, Bangalore 560 080, India
[b] DST Unit on Nanoscience, Department of Chemistry and Sophisticated Analytical Instrument Facility, Indian Institute of Technology Madras, Chennai 600 036, India

ARTICLE INFO

ABSTRACT

We have prepared tellurium (Te) and silver telluride (Ag$_2$Te) nanowires in solution and investigated their nonlinear optical transmission by the open-aperture z-scan technique, using nanosecond laser pulses, at the excitation wavelengths of 532 and 1064 nm. The nonlinearity has contributions from absorption saturation, excited state absorption and nonlinear scattering processes. The saturation intensity and nonlinear absorption coefficient are calculated numerically. Nonlinear absorption in Ag$_2$Te nanowires is found to be one order of magnitude higher than that in Te nanowires. Observation of optical limiting at both excitation wavelengths indicates the potential of these materials to be used as broadband optical limiters.

1. Introduction

Nanophotonics is emerging as a key player in novel sensing and imaging applications, as well as in the areas of advanced information technology, cryptography, and signal processing. One-dimensional nanostructured metals have attracted much attention in this regard because of their potential applications in ultrahigh-density magnetic recording, ultrafast optical switching, and microwave devices [1–4]. Propagation of surface plasmon-polariton (SPP) modes excited in an optical nanowire consisting of a chain of Ag spheres embedded in dielectric shells has been numerically investigated, and nonlinear optical phenomena such as optical switching and limiting have been found [5]. A tunable nanowire nonlinear optical probe has been reported by Nakayama et al. [6]. In order to illustrate the applicability of plasmonic nanowire waveguides to optical circuits, Leosson et al. [7] demonstrated a compact variable optical attenuator consisting of a single nanowire that simultaneously carries light and electrical current, outlining the advantage of using nanowire waveguides in specific types of integrated optical devices. Skillfully connected, small diameter nanowires of highly conductive metals may be useful for future electronic applications, e.g., conductive polymer-metal composites with low metal loading [8].

Materials exhibiting optical limiting properties are necessary for the production of photonic devices that control amplitude gain or extinction, polarization, phase, reflection and refraction of light [9]. Semiconductor-doped glasses [10,11], inorganic and hybrid nanostructures [12], organic molecules like dyes and fullerenes [13], colloidal metals and metal nanoparticles [14,15], silicon nanowires [16] and CdO nanowires [17] are some of the materials known to show good optical limiting.

The optical limiting properties of a few metal nanowires (Cu, Co, Ni, Pd, Pt and Ag) have been studied recently by Pan and colleagues [18] using 7 ns laser pulses, and results obtained at 532 and 1064 nm indicate that they have broadband optical limiting capabilities. The observed optical limiting in some of them is comparable to or better than that of carbon nanotubes, and the optical limiting is found to arise mostly from nonlinear scattering. In general, when irradiated with nanosecond duration laser pulses and heated up to the vaporization temperature, scattering is believed to occur from micro-bubbles formed by evaporation of the solvent [19–21]. Above the vaporization temperature the absorbing species produce microplasmas which scatter the light [22–25]. Since ionization usually has to be a two-photon or multiple-photon process at these excitation wavelengths, the corresponding light scattering will be nonlinear, rapidly increasing with increasing light intensity. Pong et al. [26] have reported the nonlinear optical properties of 5 nm Au nanowire intermediates formed during the synthesis of gold nanospheres. Optical second-harmonic (SH) generation from Au nanowire arrays at the fundamental photon energy of 1.17 eV also has been studied [27].

In this Letter we report the synthesis and optical limiting characteristics of Te and Ag$_2$Te nanowires. Ag$_2$Te is a semiconductor which can be doped to give both n-type and p-type properties. It has the potential to act as a photonic as well as an electronic device, which will be of significance in optoelectronic systems. Ag$_2$Te is also known to show a large magnetoresistance. We followed a chemical process for the synthesis of these anisotropic structures. Electrochemical deposition and electrophoretic deposition of high-density tellurium (Te) nanowire arrays with wire diameters of 60 nm and lengths of 15–20 μm, respectively, in

* Corresponding authors. Fax: +91 80 2361 0492 (R. Philip).
E-mail addresses: pradeep@iitm.ac.in (T. Pradeep), reji@rri.res.in (R. Philip).

nanochannels of anodic aluminum oxide (AAO) templates has been reported before [28]. The Te nanowires synthesized via electrochemical deposition (ECD) were generally single crystalline in nature with the wire longitudinal axis along the [0 0 1] direction, whereas those synthesized via electrophoretic deposition (EPD) showed polycrystalline structures with numerous tiny Te crystallites packed randomly in the wires.

2. Experimental

To synthesize the nanowires, sodium dodecyl sulfate (SDS, $C_{12}H_{25}O_4SNa$, 99%) was obtained from Acros, and tellurium dioxide (TeO_2, 99.9%) powder was purchased from Alfa Aesar. $AgNO_3$ and hydrazine monohydrate ($N_2H_4 \cdot H_2O$, 99–100%) were purchased from SD Fine Chemicals, India. The wet chemical method given by Lin et al. [29] was employed for synthesis, and deionized water was used throughout the procedure. UV–visible absorption spectra of the samples were measured using a Perkin Elmer Lambda 25 spectrophotometer. High-resolution transmission electron microscopy (HRTEM) and Energy dispersive X-ray analysis (EDAX) were
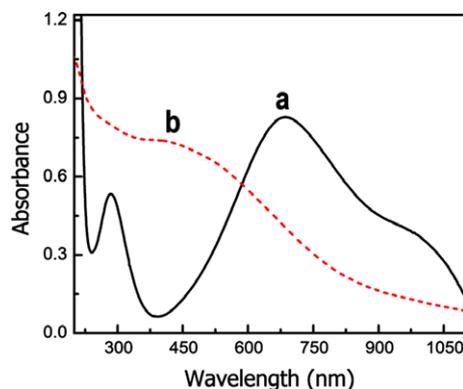
Fig. 1. UV–visible absorption spectra of (a) Te Nanowires and (b) Ag_2Te nanowires.

carried out with JEOL 3010, 300 kV instrument equipped with a UHR polepiece and an Oxford EDAX housed in TEM, respectively. The samples were prepared by dropping the dispersion on carbon coated copper grids. Scanning electron microscopy (SEM) was
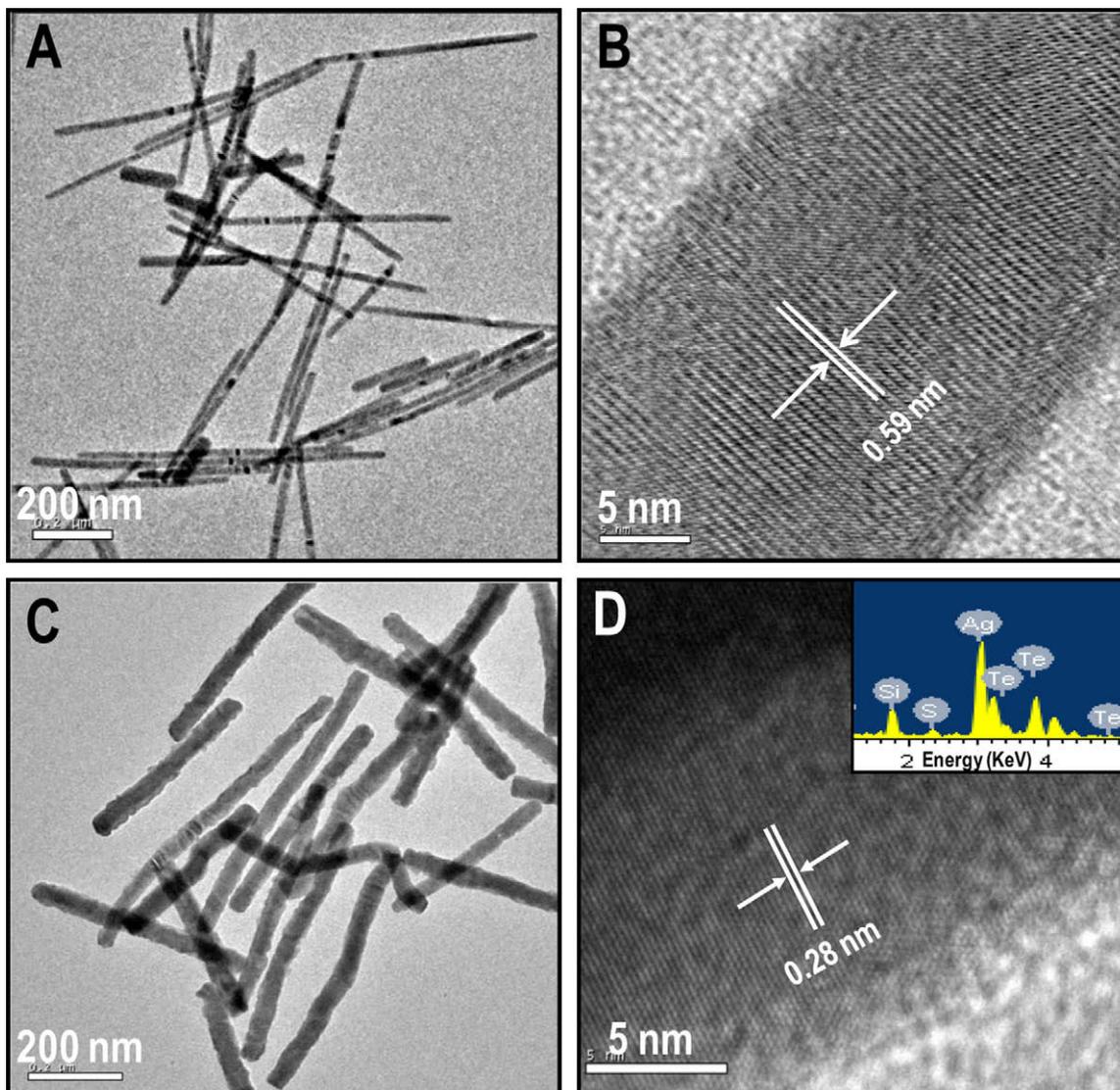
Fig. 2. (A) Large area TEM image of Te nanowires, (B) lattice resolved HRTEM image of the body of a single Te nanowire, (C) large area TEM image of Ag_2Te nanowires, and (D) lattice resolved HRTEM image of the body of a single Ag_2Te nanowire. Inset of D shows EDAX spectrum of Ag_2Te nanowires. Si and S peaks are due to the carbon substrate and SDS surfactant used in the synthesis of nanowires, respectively.

carried out using an FEI QUANTA-200 SEM instrument and the samples were prepared on conducting ITO glass plates.

To study the optical limiting properties, we employed the open-aperture z-scan experiment [30] using a Q-Switched Nd:YAG laser (Quanta Ray, Spectra Physics), at the fundamental and second harmonic excitation wavelengths of 1064 and 532 nm, respectively. The laser pulsewidths (FWHM) were approximately 9 ns at 1064 nm and 7 ns at 532 nm. The laser beam, which is spatially Gaussian, was focused using a plano-convex lens (of 20 cm focal length at 532 nm). The nanowire samples were then taken in a 1 mm glass cuvette which was mounted on a stepper motor controlled linear translation stage. The sample was translated in the z direction in small steps, and the transmitted energy was measured for each position z using a pyroelectric laser energy detector (Laser Probe Inc.). A photodiode was kept at an angle to the beam axis to measure scattered light from the sample. The experiment was automated such that laser pulses could be generated on demand. The interval between two successive laser pulses was always kept sufficiently large (typically more than 1 s), to enable the complete thermal relaxation of the sample before the arrival of the following pulse. From the z-scan data thus obtained, the input laser fluence vs. sample transmittance curves (optical limiting curves) could be plotted, and the nonlinear parameters could be calculated.

3. Results and discussion

The absorption spectrum of Te nanowires has two characteristic peaks: peak I and peak II. Peak I appears in the range of 250–350 nm, and it is due to the transition from p-bonding valence band to the p-antibonding conduction band Peak II appears around 600–850 nm, and it is due to the transition from p-lone pair valence band to the p-antibonding conduction band [29,31,32]. In this synthesis, peak I appeared at 284 nm and peak II appeared at 685 nm. Ag_2Te nanowires show a broad peak at 480 nm. The absorption spectra of the prepared Te and Ag_2Te nanowires are shown in Fig. 1. It is interesting to note that for Te nanowires the absorbance is nearly the same at the optical excitation wavelengths of 532 and 1064 nm. In general, such a feature can be advantageous in the design of broadband optical limiters.

Fig. 2A depicts a large area TEM image of Te nanowires. All the nanowires are found to be uniform. The length and width of the Te nanowires are around 600 and 20 nm, respectively. Fig. 2B shows lattice resolved HRTEM image of the body of a single nanowire.
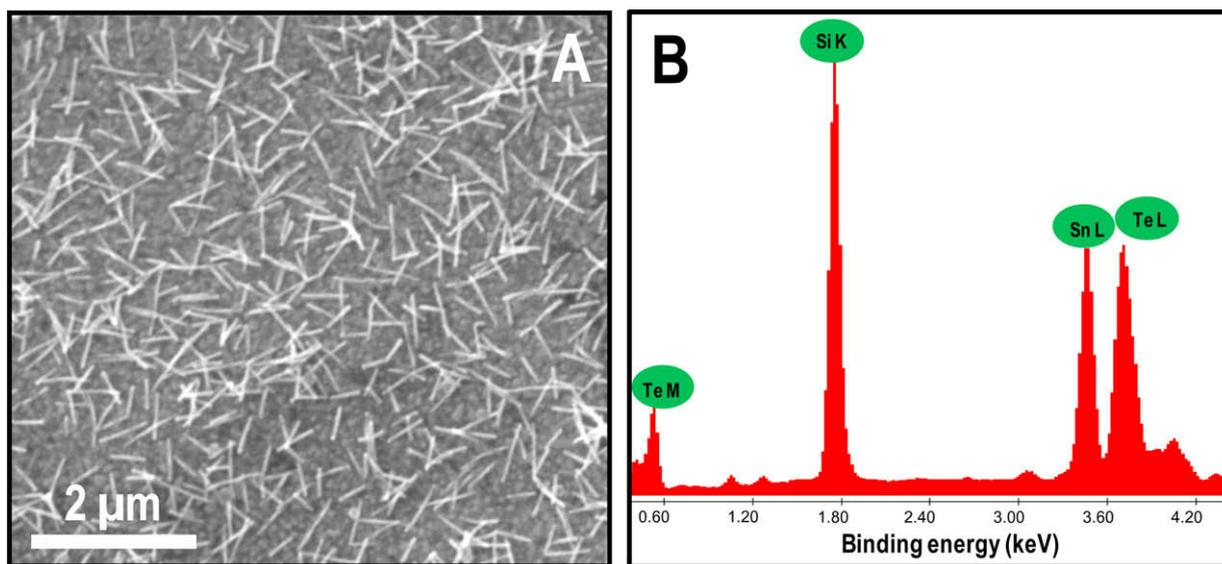
Fig. 3. (A) Large area SEM, and (B) EDAX spectrum of Te nanowires. Si and Sn peaks are due to the ITO substrate used.
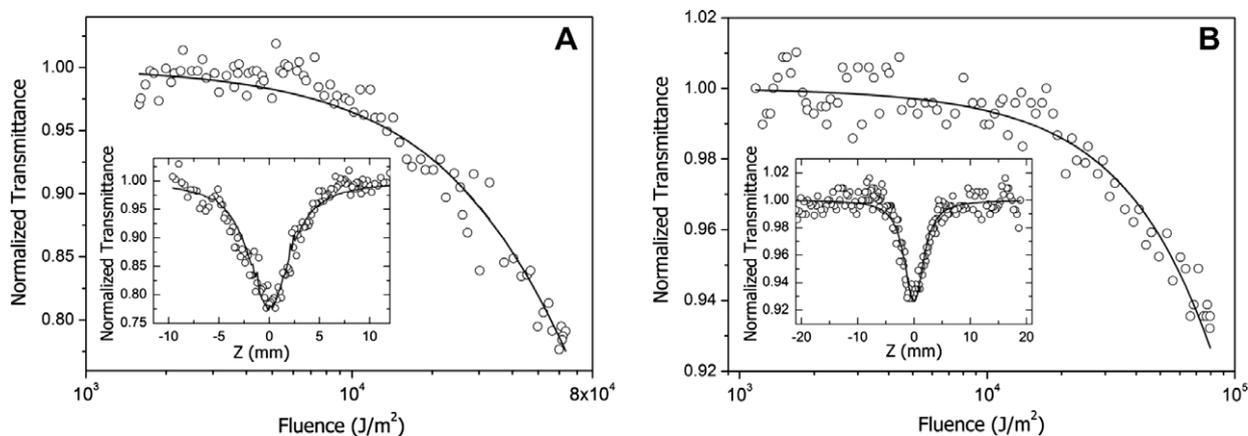
Fig. 4. Nonlinear absorption in Te nanowires at (A) 532 nm and (B) 1064 nm. Insets show the corresponding z-scan curves. Circles are data points and solid curves are numerical fits using Eq. (2).
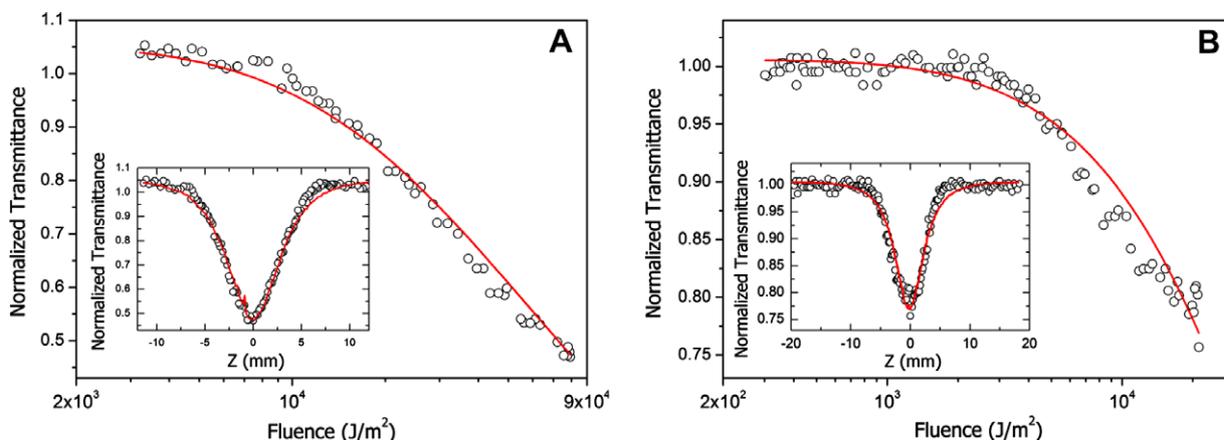
Fig. 5. Nonlinear absorption in Ag$_2$Te nanowires at (A) 532 and (B) 1064 nm. Insets show the corresponding z-scan curves. Circles are data points and the solid curves are numerical fits using Eq. (2).
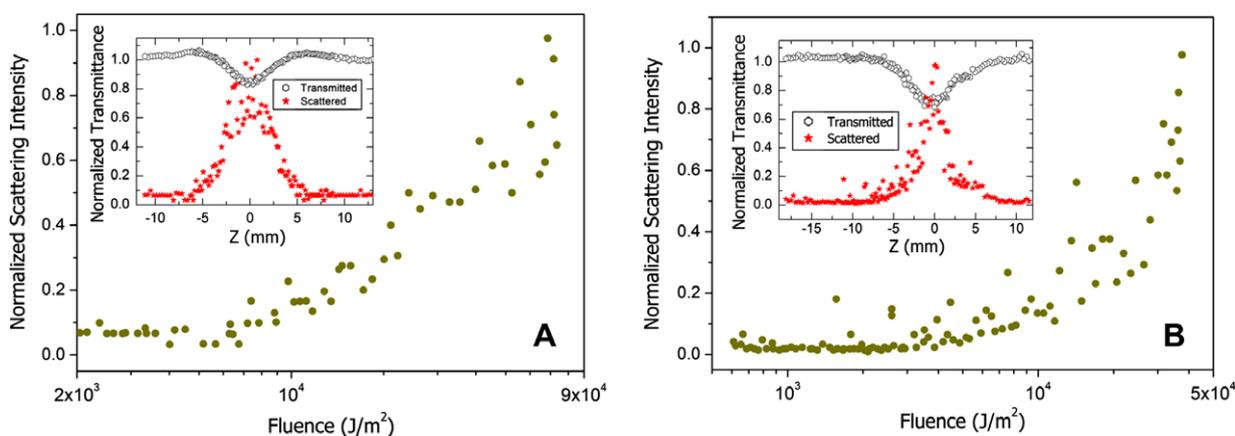
Fig. 6. Nonlinear scattering in Ag$_2$Te nanowires for excitation at (A) 532 nm and (B) 1064 nm. Scattered light was detected by an uncalibrated photodiode while transmitted light was detected by a calibrated pyroelectric detector. The scattered and transmitted intensities look comparable in the graphs because normalized quantities are used for plotting. In absolute terms, the scattered intensity seen by the photodiode is much smaller than the transmitted intensity seen by the pyroelectric detector.

Table 1
Linear and nonlinear optical properties of Te and Ag$_2$Te nanowires at the studied concentrations.

Wavelength (nm)	Te nanowire			Ag$_2$Te nanowire		
	α (m^{-1})	I_s (W/m^2)	β (m/W)	α (m^{-1})	I_s (W/m^2)	β (m/W)
532	287.68	1.6×10^{13}	3.8×10^{-11}	356.67	1.8×10^{12}	1.5×10^{-10}
1064	223.14	1.9×10^{13}	1.7×10^{-11}	261.36	2.5×10^{13}	1.6×10^{-10}

α = Linear absorption coefficient, I_s = saturation intensity and β = nonlinear absorption coefficient.

The interplanar distance is found to be 0.59 nm, corresponding to the (0 0 1) plane of Te. There are no dislocation and planar defects on the nanowires, indicating that these are single crystalline. Fig. 2C shows the large area TEM image of Ag$_2$Te nanowires and Fig. 2D shows the lattice resolved HRTEM image of the body of a single Ag$_2$Te nanowire. The interplanar spacing is found to be 0.28 nm, corresponding to the (2 2 0) lattice plane of Ag$_2$Te nanowire. Inset of D shows the EDAX spectrum of Ag$_2$Te which confirms the presence of silver. Fig. 3A and B shows the large area SEM and EDAX spectrum of Te nanowires, respectively.

Fig. 4A and B shows the optical limiting curves obtained for Te nanowires for 532 and 1064 nm excitation, respectively. Fig. 5A and B is similar figures for Ag$_2$Te nanowires. At 1064 nm excitation

the limiting is relatively weaker in both cases. In general, optical limiting behavior of a medium can have contributions from effects such ESA (including excited singlet or triplet absorption, free-carrier absorption etc.), two- or three-photon absorption (2PA, 3PA), self-focusing/defocusing, thermal blooming, and nonlinear scattering. Similar to the previous observation by Pan et al. [18] in other metal nanowires, we too noticed nonlinear scattering from the present Te and Ag$_2$Te samples (Fig. 6A and B). However it was relatively weaker in comparison to the nonlinear absorption, which became evident while trying to fit experimental data to the standard nonlinear transmission equations. It turned out that there are two predominant causes for the nonlinearity: one is a saturation of the ground state absorption, and the other is an

Table 2
Effective two-photon absorption coefficients reported in literature for metal and semiconductor nanoparticles. All values are for a laser excitation wavelength of 532 nm, using pulses of 5–10 ns duration.

Sample	β (m/W)
Te nanowires [present work]	3.8×10^{-11}
Ag$_2$Te nanowires [present work]	1.5×10^{-10}
Ag nanoparticles [37]	$\sim 10^{-10}$
Au nanorods [38]	5.3×10^{-11}
Cu nanocomposite glass [34]	8.4×10^{-11}
CdS quantum dots [39]	3.15×10^{-10}
Bi nanorods [33]	5.3×10^{-11}
ZnO nanoparticles [40]	2.1×10^{-11}
SWNT [41]	2.46×10^{-11}
CdO nanowires [17]	5.93×10^{-10}
C$_{60}$ [41]	3.28×10^{-11}

absorption by the excited state (saturable absorption is more obvious in the additional z-scans curves given in supporting information). Therefore an effective nonlinear absorption coefficient $\alpha(I)$, given by

$$\alpha(I) = \frac{\alpha_0}{1 + \left(\frac{I}{I_s}\right)} + \beta I \tag{1}$$

can be considered, where α_0 is the unsaturated linear absorption coefficient at the wavelength of excitation, I is the input laser intensity, and I_s is the saturation intensity (intensity at which the linear absorption drops to half its original value). $\beta I = \sigma N$ is the excited state absorption (ESA) coefficient, where σ is the ESA cross section and $N(I)$ is the intensity-dependent excited state population density. For calculating the transmitted intensity for a given input intensity, the propagation equation,

$$\frac{dI}{dz'} = -\left[\left(\alpha_0 \bigg/ \left(1 + \frac{I}{I_s}\right)\right) + \beta I\right] I \tag{2}$$

was numerically solved. Here z' indicates the propagation distance within the sample. By determining the best-fit curves for the experimental data, the nonlinear parameters could be calculated, which are given in Table 1. It is seen that for both excitation wavelengths, while β is in the order of 10^{-11} m/W for Te, it is one order of magnitude higher at 10^{-10} m/W for Ag$_2$Te. Thus an obvious enhancement in the nonlinearity has been achieved from the presence of nano Ag in the composite. In comparison, when excited using 7 ns laser pulses at 532 nm, the β value for Bi nanorods was around 10^{-11} m/W [33], Cu nanocomposite glasses was between 10^{-12} and 10^{-10} m/W [34], Au–Ag core–shell nanoparticles was between 10^{-10} and 10^{-9} m/W [35], and CdS quantum dots was at 10^{-9} m/W [36]. A comparison of the obtained values to the effective two-photon absorption coefficients reported in literature for a few other metal and semiconductor nanoparticles is given in Table 2. Since β values are not given in Ref. [18] a direct comparison could not be made, but from the optical limiting curves given therein, it appears that the optical limiting efficiency of the present samples is somewhat lower. We believe that this is a consequence of the lower nonlinear scattering seen in the Ag and Ag$_2$Te nanowires.

4. Conclusions

In conclusion, we have prepared Te and Ag$_2$Te nanowires and investigated their nonlinear optical transmission properties at 532 and 1064 nm excitation wavelengths. The nanowires are found to have long-term stability under laser irradiation. Excited state absorption is found to be the major contributor to the observed optical limiting, with a relatively minor contribution from nonlinear scattering. The nonlinear absorption coefficient measured in Ag$_2$Te nanowires is one order of magnitude larger than that in Te nanowires. These values are comparable to the values obtained earlier in certain other metal and semiconductor nanosystems. Observation of optical limiting at both wavelengths indicates the potential of these samples to be used as broadband optical limiters.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2009.12.065.

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