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Abstract: Several different compositions of tellurium-thallium oxide glasses were fabricated and tested for their Raman gain performance. The addition of PbO to the glass matrix increased the surface optical damage threshold by 60-230%. The maximum material Raman gain coefficient experimentally obtained was (58 ± 3) times higher than the peak Raman gain of a 3.18 mm thick Corning 7980-2F fused silica sample ($\Delta v = 13.2$ THz). The highest peak in the Raman gain spectrum of the tellurium-thallium glass is attributed to the presence of TeO_3 and TeO_{3+1} structural units with thallium ions in the vicinity at a frequency shift near 21.3 THz.

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1. Introduction

Raman amplification is an important technology that has made an impact on currently deployed commercial optical transmission systems. Current transmission systems use distributed Raman amplification in order to improve the noise figure [1]. Discrete Raman amplification is used in the form of germanium-doped silica fibers that also serve as dispersion compensation devices [2]. However, all of these devices utilize silica-based fibers, and it is well known that silicates are one of the weakest nonlinear glasses for Raman gain [3]. Theoretical predictions and Raman scattering experiments have been made on both oxide and non-oxide glasses to find materials that exhibit higher nonlinearities than silicates [4-6]. Chalcogenide glass is known to have the highest non-resonant nonlinearities of all glasses, but it also has high attenuation coefficients (on the order of meter^{-1}) and low optical damage thresholds [7-10]. Tellurite glass has been thoroughly researched in terms of the role of its structure on optical nonlinearities and these glasses have exhibited some of the highest nonlinearities in oxide glasses known to date [11-22]. It has been shown that introducing thallium into a tellurite glass matrix can further increase the nonlinearity [12,20,21]. Here we report on the impact on the Raman gain by varying the tellurium to thallium ratio in a binary glass, and also the impact of adding PbO to the matrix for both Raman gain and surface optical damage threshold enhancement.

2. Glass elaboration

Glassy pellets were prepared by first melting the appropriate quantities of reagent grade chemicals - PbO (Aldrich, 99.5%), TeO_2 (prepared by decomposition at 550°C of commercial H_6TeO_6 (Aldrich, 99.9%)) and Tl_2TeO_3 (synthesised by heating at 350°C for 18 hours an intimate mixture of TeO_2 and Tl_2CO_3 under a nitrogen atmosphere) in platinum crucibles for half an hour at 800°C. The melts were then quickly quenched by flattening between two brass blocks separated by a brass ring to obtain cylindrical samples 10 mm wide and 1-3 mm thick and a cooling rate of about 10^{4}°K/s was utilized.

Seven samples from two different families (TeO_2-$TlO_{0.5}$ and TeO_2-$TlO_{0.5}$-PbO) were prepared using this technique. Figure 1 displays the dispersion in the absorption coefficient measured with a Cary 500 spectrophotometer for the tellurite glasses in this paper and in [18]. The samples were optically polished to allow optical beams of 125 μm beam waist to pass through 1-3 mm of the glass with minimum scattering. The glasses reported in [12,30] and reported here were fabricated by the same research group. The density, glass transition and crystallization temperatures, and thermal stability of the different glass samples have been reported elsewhere [22-24].
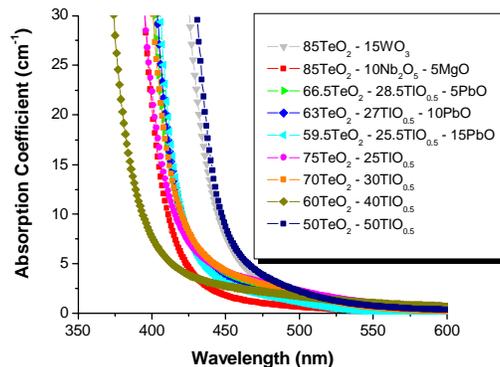

Fig. 1. Dispersion in the absorption coefficient for the tellurite glasses tested for Raman gain.

3. Experimental procedure

The procedure to test for Raman gain in bulk glass samples has been reported previously and further clarification is currently being provided [18,25]. In summary, picosecond pulses of high irradiance at 1064 nm are used as a pump source and a wavelength tunable source from an OPG/OPA is used as the amplified probe. A femtosecond source was avoided because the response time of the Raman vibrations is reported to be on the order of hundreds of femtoseconds [26,27]. Since Raman gain is primarily a polarization-sensitive process, the probe is linearly polarized 45^0 with respect to the linear pump polarization. The polarization of the probe beam parallel to the pump beam polarization is used to detect approximately 10% gain, while the polarization of the probe beam orthogonal to the pump beam polarization is the "effective" input energy. The depolarization ratio (VV/VH) - obtained from spontaneous Raman scattering experiments on the same glasses - is used as a correction factor since the probe beam polarization orthogonal to the pump beam polarization does experience minor Raman excitations in these glasses [11]. After propagation through the sample a monochromator is used to filter the pump from the probe wavelength, and the two probe polarizations enter two identical, calibrated germanium detectors via a polarizing beam splitter. In concert with a calibrated silicon detector for the 1064 nm pump, Raman gain can be measured on a shot-to-shot basis, and averaging is done over hundreds of shots. An in-depth overview of this approach and procedure will be provided in [25]. The experimental apparatus is calibrated on a 3.18mm thick Corning 7980-2F fused silica sample (peak Raman gain = 1.1 x 10^{-13} m/W in good agreement with published values), and corrections are made for Fresnel reflections at the surfaces with the corresponding index of refraction data and depolarization ratio [28,29]. The Raman gain data published in [18] have been compared to cross-section calculations based on spontaneous Raman scattering experiments and have shown to be in good agreement for the $\Delta v = 20$ THz frequency shift studied [19].

4. Results and interpretation

The measured Raman gain values have been overlaid with the spontaneous Raman scattering spectra for the three TeO_2-$TlO_{0.5}$-PbO glasses investigated. The spontaneous Raman spectra were obtained using a 90^0 scattering configuration with an excitation wavelength of 780 nm to obtain scattering data at a wavelength much longer than the band edges. The decrease in the spontaneous Raman data at low frequency shifts in Fig. 2 is caused by the cut-off of the notch filter used to discriminate the spontaneous Raman scattering from Rayleigh scattering. The Bose-Einstein correction factor has been applied to the spontaneous Raman scattering data. Figure 2(a) displays a peak experimentally obtained Raman gain coefficient of (42 ± 1.5) times that of the Corning 7290 fused silica sample for the composition $59.5TeO_2 - 25.5TlO_{0.5} - 15PbO$. Figure 2(b) demonstrates the Raman gain curve for $63TeO_2 - 27TlO_{0.5} - 10PbO$, and Fig. 2(c) shows the Raman gain curve for $66.5TeO_2 - 28.5TlO_{0.5} - 5PbO$. Table 1 illustrates how the peak at $\Delta v = 20$ THz caused by the vibrations of the TeO_4 units and the peak at $\Delta v = 21.3$ THz caused by the vibrations of the TeO_3 and TeO_{3+1} units vary with molar concentration within the glass matrix, and lists the measured optical surface damage thresholds. It is not yet known why the addition of PbO to the glass matrix increases the surface optical damage threshold over the binary TeO_2-$TlO_{0.5}$ glasses based on previous analysis of identical compositions [30]. However, we believe it is related to the role of PbO as a network participant in the ternary glasses. While lead is known to act as a modifier in very small molar quantities, it can serve as an intermediate or partner former in some glass compositions. The addition to the glass in the previous role would allow the average bond strength of the glass to be enhanced, thus "hardening" the material's laser damage resistance. A systematic study to evaluate this trend in these and other glass systems is necessary to validate these structure-based assumptions.
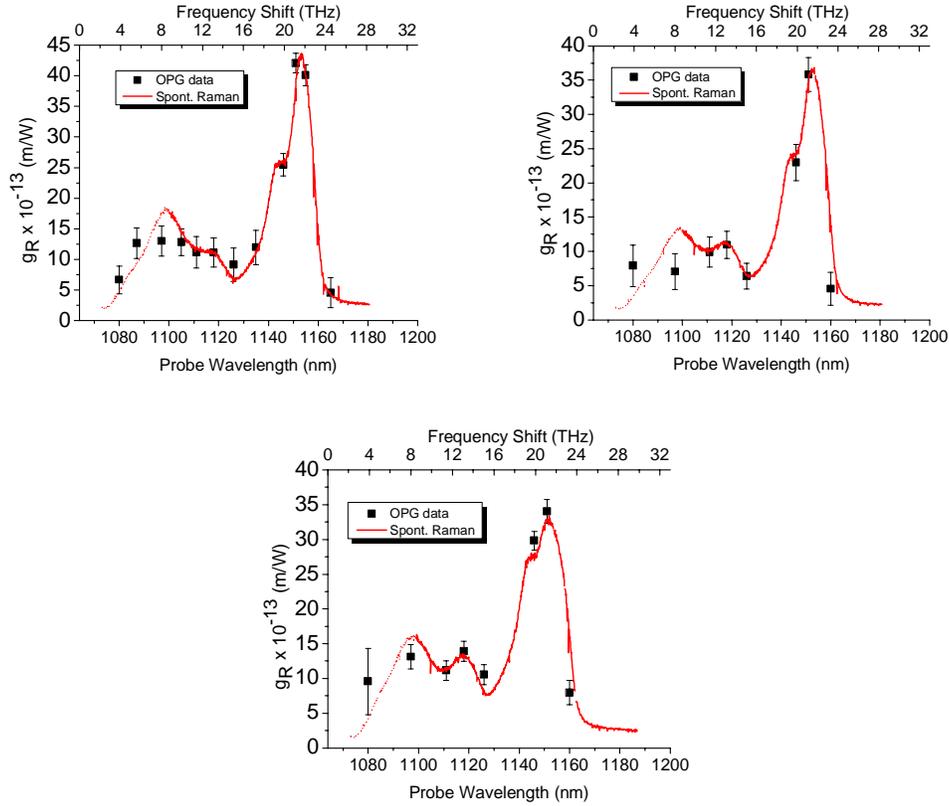
Figs. 2. (a), (b), and (c). Raman gain curve of (a) $59.5TeO_2 - 25.5TlO_{0.5} - 15PbO$, (b) $63TeO_2 - 27TlO_{0.5} - 10PbO$, and (c) $66.5TeO_2 - 28.5TlO_{0.5} - 5PbO$

Table 1. Raman gain coefficients of TeO_4 (Δv = 20 THz) units and TeO_3 and/or TeO_{3+1} units (Δv = 21.3 THz) resonances and optical surface damage thresholds

Glass Composition (Molar Percent)	Δv = 20 THz Gain coef. (10^{-13} m/W)	Δv = 21.3 THz Gain coef. (10^{-13} m/W)	Optical surface damage threshold (GW/cm^2)
$66.5TeO_2 - 28.5TlO_{0.5} - 5PbO$	30 ± 1.5	34 ± 1.7	8.5
$63TeO_2 - 27TlO_{0.5} - 10PbO$	23 ± 2.6	38 ± 2.5	8.5
$59.5TeO_2 - 25.5TlO_{0.5} - 15PbO$	25 ± 2	42 ± 1.5	8.3
$75TeO_2 - 25\ TlO_{0.5}$	25 ± 4	19 ± 3	3.6
$70TeO_2 - 30TlO_{0.5}$	21 ± 4	23 ± 5	4.4
$60TeO_2 - 40TlO_{0.5}$	21 ± 5	30 ± 7	4.0
$50TeO_2 - 50TlO_{0.5}$	19 ± 3	58 ± 3	5.1

The damage threshold of the binary TeO_2-$TlO_{0.5}$ glasses was low enough to produce unreliable data off of the main Δv = 20 THz and Δv = 21.3 THz peaks in the Raman gain spectrum. Most attempts to measure Raman gain away from these main peaks resulted in surface optical damage after less than five minutes of exposure to the 10 Hz system. Nevertheless, Raman gain measurements were made over the Δv = 20 THz and Δv = 21.3 THz bands for all four binary compositions and agree with structural variation analysis of these glasses [11,12,19-21].

In essence, a tellurium rich glass contains many TeO_4 disphenoids with the lone pair electrons so directed as to constitute the third equatorial corner of a TeO_4E trigonal

bipyramid; these are the most polarizable entities in the glass network and are responsible for the $\Delta v = 20$ THz vibration as shown by *ab initio* calculations [31]. By combining another structural unit to the glass matrix that also has a Lewis ns^2 lone pair, it can be anticipated that the nonlinearity of the glass can increase due to strengthened stereochemical activity [11,12]. Addition of a third species which contains a Lewis ns^2 lone pair, in this case PbO, has also shown to further increase the purely electronic third order nonlinearity n_2 in these glasses [29]. As the mole % of tellurium decreases, the TeO_4 units distort to form TeO_{3+1} units and then to TeO_3 units, which have vibrational resonances at a frequency shift near 21.3 THz. This last large resonance, which is stronger than the TeO_4 vibrational resonance in these glasses, should be related to the presence of thallium ions in the vicinity of the TeO_3 and TeO_{3+1} units. In this frequency range, no Raman band could be related to the presence of thallium oxide groups. NMR investigations are ongoing to evaluate the thallium ions environment in these glasses.

As the ratio of tellurium oxide to thallium oxide is varied, the $\Delta v = 20$ THz and $\Delta v = 21.3$ THz bands vary in terms of strength in the Raman gain curve. A peak Raman gain coefficient of (58 ± 3) times that of the peak Raman gain of the fused silica sample is reported for the binary sample containing 50% mole of $TlO_{0.5}$. This represents the highest *directly* measured and reported peak Raman gain coefficient to date in oxide glasses known to the authors. With the band edges below 500 nm for all of the samples tested, it is reasonable to expect similar performance at the telecommunication wavelengths of 1280-1625 nm because the Raman gain measurements were made with 1064 nm pumping which avoids any resonantly enhanced Raman effects. Furthermore, the increased peak Raman gain coefficient with increasing thallium oxide content reported here shows a trend of increasing non-resonant nonlinearity with increasing thallium content in the glass matrix, in partial agreement with the trend listed in Table 1 in [30] for purely real electronic $\chi^{(3)}$ measurements. The reasons for some of the discrepancies reported in this work and in [30] are currently being investigated.

5. Conclusion

Several tellurium-thallium oxide glass compositions were fabricated and tested for their performance as a candidate for development into Raman amplifiers. Compositions rich in thallium oxide content exhibited the highest directly measured peak Raman gain coefficients for oxide glasses to date. Addition of PbO to the glass matrix significantly increased the optical surface damage threshold of the glass, a necessary criteria for materials to be used in high power Raman applications. The trends in the Raman gain data are in partial agreement with n_2 measurements made on separate TeO_2-$TlO_{0.5}$ glasses as compared to fused silica.