1-1-2005

Raman gain measurements of thallium-tellurium oxide glasses

Robert Stegeman

University of Central Florida

Clara Rivero

University of Central Florida

Kathleen Richardson

University of Central Florida

George Stegeman

University of Central Florida

Peter Delfyett Jr.

*University of Central Florida*Find similar works at: <https://stars.library.ucf.edu/facultybib2000>University of Central Florida Libraries <http://library.ucf.edu>

This Article is brought to you for free and open access by the Faculty Bibliography at STARS. It has been accepted for inclusion in Faculty Bibliography 2000s by an authorized administrator of STARS. For more information, please contact STARS@ucf.edu.

Recommended Citation

Stegeman, Robert; Rivero, Clara; Richardson, Kathleen; Stegeman, George; Delfyett, Peter Jr.; Guo, Yu; Pope, April; Schulte, Alfons; Cardinal, Thierry; Thomas, Philippe; and Champarnaud-Mesjard, Jean-Claude, "Raman gain measurements of thallium-tellurium oxide glasses" (2005). *Faculty Bibliography 2000s*. 5697.

<https://stars.library.ucf.edu/facultybib2000/5697>

Authors

Robert Stegeman, Clara Rivero, Kathleen Richardson, George Stegeman, Peter Delfyett Jr., Yu Guo, April Pope, Alfons Schulte, Thierry Cardinal, Philippe Thomas, and Jean-Claude Champarnaud-Mesjard

Raman gain measurements of thallium-tellurium oxide glasses

Robert Stegeman, Clara Rivero, Kathleen Richardson, George Stegeman, and Peter Delfyett Jr.

*College of Optics and Photonics, University of Central Florida
Orlando, FL 32816-2700
steg@creol.ucf.edu*

Yu Guo, April Pope, and Alfons Schulte

*Department of Physics, University of Central Florida
Orlando, FL 32816-1390*

Thierry Cardinal

*Institut de Chimie de la Matière Condensée de Bordeaux
87 Avenue du Dr. Albert Schweitzer, 33608 Pessac cedex, France*

Philippe Thomas and Jean-Claude Champarnaud-Mesjard

*Science des Procédés Céramiques et Traitements de Surfaces, Faculté des Sciences et Techniques
123 Avenue Albert Thomas, 87060 Limoges cedex, France*

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 ($\Delta\nu = 13.2$ 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.

© 2005 Optical Society of America

OCIS codes: (160.4330) Nonlinear optical materials; (060.2320) Fiber optics amplifiers and oscillators; (190.5650) Raman effect; (190.5890) Scattering, stimulated

References and links

1. M.N. Islam, "Raman Amplifiers for Telecommunications," IEEE J. Sel. Top. Quantum Electron. **8**, 548-559 (2002).
2. P. B. Hansen, G. Jacobovitz-Veselka, L. Grüner-Nielsen, A. J. Stentz, "Raman amplification or loss compensation in dispersion compensating fibre modules," Electron. Lett. **34**, 1136-1137 (1998).
3. F.L. Galeener, J. C. Mikkelsen Jr., R. H. Geils, W. J. Mosby, "The relative Raman cross sections of vitreous SiO_2 , GeO_2 , B_2O_3 , and P_2O_5 ," Appl. Phys. Lett. **32**, 34-36 (1978).
4. M. E. Lines, "Raman gain estimates for high-gain optical fibers," J. Appl. Phys. **62**, 4363-4370 (1987).
5. A. E. Miller, K. Nassau, K. B. Lyons, M. E. Lines, "The intensity of Raman scattering in glasses containing heavy metal oxides," J. Non-Cryst. Solids **99**, 289-307 (1988).
6. M. E. Lines, "Oxide glasses for fast photonic switching: A comparative study," J. Appl. Phys. **69**, 6876-6884 (1991).
7. K. A. Richardson, T. M. McKinley, B. Lawrence, S. Joshi, A. Villeneuve, "Comparison of nonlinear optical properties of sulfide glasses in bulk and thin film form," Opt. Mater. **10**, 155-159 (1998).
8. J. M. Harbold, F. Ö. Ilday, F. W. Wise, J. S. Sanghera, V. Q. Nguyen, L. B. Shaw, I. D. Aggarwal, "Highly nonlinear As-S-Se glasses for all-optical switching," Opt. Lett. **27**, 119-121 (2002).

9. P. A. Thielen, L. B. Shaw, P. C. Pureza, V. Q. Nguyen, J. S. Sanghera, I. D. Aggarwal, "Small-core As-Se fiber for Raman amplification," *Opt. Lett.* **28**, 1406-1408 (2003).
10. R. Slusher, G. Lenz, J. Hodelin, J. Sanghera, L. Brandon Shaw, I. D. Aggarwal, "Large Raman gain and nonlinear phase shifts in high-purity As₂Se₃ chalcogenide fibers," *J. Opt. Soc. Am. B* **21**, 1146-1155 (2004).
11. T. Sekiya, N. Mochida, A. Ohtsuka, M. Tonokawa, "Raman spectra of MO_{1/2}-TeO₂ (M=Li, Na, K, Rb, Cs, and Tl) glasses," *J. Non-Cryst. Solids* **144**, 128-144 (1992).
12. B. Jeansannetas, S. Blanchandin, P. Thomas, P. Marchet, J. C. Champarnaud-Mesjard, T. Merle-Mejean, B. Frit, V. Nazabal, E. Fargin, G. Le Flem, M. O. Martin, B. Bosquet, L. Canioni, S. Le Boiteux, P. Segonds, L. Sarger, "Glass structure and optical nonlinearities in thallium(I) tellurium (IV) oxide glasses," *J. Sol. St. Chem.* **146**, 329-335 (1999).
13. J. S. Wang, E. M. Vogel, F. Snitzer, "Tellurite glass: a new candidate for fiber devices," *Opt. Mat.* **3**, 187-203 (1994).
14. A. Mori, H. Masuda, K. Shikano, K. Oikawa, K. Kato, M. Shimizu, "Ultra-wideband tellurite-based Raman fiber amplifier," *Electron. Lett.* **37**, 1142-1143 (2001).
15. V. V. Ravi Kanth Kumar, A. K. George, J. C. Knight, P. St. J. Russell, "Tellurite photonic crystal fiber," *Opt. Express* **11**, 2641-2645 (2003).
16. G. Dai, F. Tassone, A. L. Bassi, V. Russo, C. E. Bottani, F. D'Amore, "TeO₂-based glasses containing Nb₂O₅, TiO₂, and WO₃ for discrete Raman fiber amplification," *Photon. Technol. Lett.* **16**, 1011-1013 (2004).
17. V. G. Plotnichenko, V. V. Koltashev, V. O. Sokolov, E. M. Dianov, I. A. Grishin, M. F. Churbanov, "Raman band intensities of tellurite glasses," manuscript in preparation.
18. R. Stegeman, L. Jankovic, H. Kim, C. Rivero, G. Stegeman, K. Richardson, P. Delfyett, Y. Guo, A. Schulte, T. Cardinal, "Tellurite glasses with peak absolute Raman gain coefficients up to 30 times that of fused silica," *Opt. Lett.* **28**, 1126-1128 (2003).
19. C. Rivero, K. Richardson, R. Stegeman, G. Stegeman, T. Cardinal, E. Fargin, M. Couzi, V. Rodriguez, "Quantifying Raman Gain Coefficients in Tellurite Glasses," *J. of Non-Cryst. Solids* **345-356**, 396-401 (2004).
20. J. Dexpert-Ghys, B. Pirio, S. Rossignol, J. M. Réau, B. Tanguy, J. J. Videau, J. Portier, "Investigations by Raman scattering of the [TeO₂-RMO_{0.5}] (M = Ag or Tl) glasses and of the related ionic conductors [TeO₂-RMO_{0.5}]_(1-x)[AgI]_x," *J. Non-Cryst. Solids* **170**, 167-174 (1994).
21. B. Jeansannetas, P. Thomas, J. C. Champarnaud-Mesjard, B. Frit, "Crystal structure of Tl₂Te₃O₇," *Mat. Res. Bull.* **32** (1), 51-58 (1997).
22. B. Jeansannetas, P. Marchet, P. Thomas, J. C. Champarnaud-Mesjard, B. Frit, "New investigations within the TeO₂-rich part of the Tl₂O-TeO₂ system," *J. of Mat. Chem.* **8** (4), 1039-1042 (1998).
23. B. Jeansannetas, "Synthèse et caractérisation de quelques phases cristallisées et vitreuses du ternaire thallium-tellure-oxygène: vers de nouveaux matériaux pour l'optique nonlinéaire," Thesis (University of Limoge 1998).
24. M. Dutreilh-Colas, "Nouveaux matériaux pour l'optique nonlinéaire: synthèse et étude structurale de quelques phases cristallisées et vitreuses appartenant aux systèmes TeO₂-Tl₂O-Ga₂O₃ et TeO₂-Tl₂O-PbO," Thesis (University of Limoges 2001).
25. R. Stegeman, C. Rivero, L. Jankovic, H. Kim, K. Richardson, G. Stegeman, P. Delfyett, Jr., "Raman gain measurements in bulk glass samples," manuscript in preparation.
26. R. H. Stolen, J. P. Gordon, W. J. Tomlinson, H. A. Haus, "Raman response function of silica-core fibers," *J. Opt. Soc. Am. B* **6**, 1159-1166 (1989).
27. I. Kang, T. Krauss, F. Wise, "Sensitive measurement of nonlinear refraction and two-photon absorption by spectrally resolved two-beam coupling," *Opt. Lett.* **22**, 1077-1079 (1997).
28. R. H. Stolen and E. P. Ippen, "Raman gain in glass optical waveguides," *Appl. Phys. Lett.* **22**, 273-276 (1972).
29. R. Hellwarth, J. Cherlow, T.-T. Yang, "Origin and frequency dependence of nonlinear optical susceptibilities of glasses," *Phys. Rev. B* **11**, 964- 967 (1975).
30. M. Dutreilh-Colas, P. Thomas, J. C. Champarnaud-Mesjard, E. Fargin "New TeO₂ based glasses for nonlinear optical applications: study of the Tl₂O-TeO₂-Bi₂O₃, Tl₂O-TeO₂-PbO and Tl₂O-TeO₂-Ga₂O₃ systems," *Phys. Chem. Glasses* **44**, 349-352 (2003).
31. A. Berthereau, E. Fargin, A. Villezusanne, R. Olazcuaga, G. Le Flem, L. Ducasse, "Determination of local geometries around tellurium in TeO₂-Nb₂O₅ and TeO₂-Al₂O₃ oxide glasses by XANES and EXAFS: investigation of electronic properties of evidenced oxygen clusters by *ab initio* calculations," *J. Sol. St. Chem.* **126**, 143-151 (1996).

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 10^4K/s was utilized.

Seven samples from two different families ($\text{TeO}_2\text{-TlO}_{0.5}$ and $\text{TeO}_2\text{-TlO}_{0.5}\text{-PbO}$) 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 $125\text{ }\mu\text{m}$ 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° 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 = 1.1×10^{-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 $\Delta\nu = 20$ 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 $\text{TeO}_2\text{-TiO}_{0.5}\text{-PbO}$ glasses investigated. The spontaneous Raman spectra were obtained using a 90° 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 $59.5\text{TeO}_2 - 25.5\text{TiO}_{0.5} - 15\text{PbO}$. Figure 2(b) demonstrates the Raman gain curve for $63\text{TeO}_2 - 27\text{TiO}_{0.5} - 10\text{PbO}$, and Fig. 2(c) shows the Raman gain curve for $66.5\text{TeO}_2 - 28.5\text{TiO}_{0.5} - 5\text{PbO}$. Table 1 illustrates how the peak at $\Delta\nu = 20$ THz caused by the vibrations of the TeO_4 units and the peak at $\Delta\nu = 21.3$ 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 $\text{TeO}_2\text{-TiO}_{0.5}$ 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) 59.5TeO₂ – 25.5TiO_{0.5} – 15PbO, (b) 63TeO₂ – 27TiO_{0.5} – 10PbO, and (c) 66.5TeO₂ – 28.5TiO_{0.5} – 5PbO

Table 1. Raman gain coefficients of TeO₄ ($\Delta\nu = 20$ THz) units and TeO₃ and/or TeO₃₊₁ units ($\Delta\nu = 21.3$ THz) resonances and optical surface damage thresholds

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

The damage threshold of the binary TeO₂-TiO_{0.5} glasses was low enough to produce unreliable data off of the main $\Delta\nu = 20$ THz and $\Delta\nu = 21.3$ 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 $\Delta\nu = 20$ THz and $\Delta\nu = 21.3$ 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 TeO₄ disphenoids with the lone pair electrons so directed as to constitute the third equatorial corner of a TeO₄E trigonal

bipyramid; these are the most polarizable entities in the glass network and are responsible for the $\Delta\nu = 20$ 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 $\Delta\nu = 20$ THz and $\Delta\nu = 21.3$ 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 $\text{TlO}_{0.5}$. 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 - $\text{TlO}_{0.5}$ glasses as compared to fused silica.

Acknowledgments

This work was carried out with the support of numerous research, equipment, and educational grants, including NSF grants ECS-0123484, ECS-0225930, and NSF Integrative Graduate Education and Research Training (IGERT) grant DGE-0114418. The US authors also acknowledge the assistance and financial support of the College of Optics and Photonics and the Student Government Association (SGA) at the University of Central Florida, as well as an equipment donation from JDS Uniphase. The work in France was supported by NSF-CNRS # 13050. Special thanks to David Morgan for the fruitful discussions and assistance in the laboratory.