

Raman band intensities of tellurite glasses

V. G. Plotnichenko, V. O. Sokolov, V. V. Koltashev, and E. M. Dianov

Fiber Optics Research Center at the A. M. Prokhorov General Physics Institute, Russian Academy of Sciences,
38 Vavilov Street, 119991 Moscow, Russia

I. A. Grishin and M. F. Churbanov

Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences, 49 Tropinin Street, 603600 Nizhny
Novgorod, Russia

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Raman spectra of TeO₂-based glasses doped with WO₃, ZnO, GeO₂, TiO₂, MoO₃, and Sb₂O₃ are measured. The intensity of bands in the Raman spectra of MoO₃-TeO₂ and MoO₃-WO₃-TeO₂ glasses is shown to be 80–95 times higher than that for silica glass. It is shown that these glasses can be considered as one of the most promising materials for Raman fiber amplifiers. © 2005 Optical Society of America

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Because of their strong nonlinear properties and capacity for doping with high concentrations of rare-earth elements, TeO₂-based glasses are now considered to be one of the most promising materials for the development of high-performance laser sources, amplifiers, and converters of radiation for the visible, near-, and mid-IR spectral ranges. Thus one can see the feasibility of using active elements from these glasses in both conventional and fiber forms.^{1,2} Large second-order optical nonlinearity of tellurite glasses has also been demonstrated.³

Wideband amplifiers based on stimulated Raman scattering (SRS) are considered to be one of the most promising trends for tellurite glass application. A tellurite fiber amplifier was developed with a 160-nm spectral band (from 1490 to 1650 nm) and a gain coefficient of 10 dB, covering almost the total S-, C-, and L-band regions of minimum optical losses for silica-based fibers.⁴ Optimization of parameters of optical fibers used in fiber Raman amplifiers is aimed at enhancing intensity and broadening and flattening the gain coefficient spectrum.

At present several tens of tellurite glasses with two, three, or more components are known that, in principle, can be used to make Raman amplifiers. However, lack of data on the spectral dependence of the stimulated Raman gain coefficient prevents the determination of the most promising structures of glasses among them. To our knowledge, the Raman gain coefficient was measured in only one study² for two compositions of tellurite glass, 15WO₃-85TeO₂ and 5 MgO-10 NbO₅-85 TeO₂, with the maximal values shown to exceed those for silica glass by 20 and 30 times, respectively. Direct measurements of the gain spectra are rather complex and require special equipment. For this purpose, measurements of spontaneous Raman scattering spectra seem to be much easier and quicker and provide a higher signal-to-noise ratio. This allows us to determine the spontaneous Raman scattering cross section, from which we can calculate the SRS gain coefficient and thus determine the most suitable composition of glass.^{6–9}

In our work we measured the spontaneous Raman spectra of glasses from various tellurite systems with

the widest and most intensive Raman bands. Samples for testing were 1-mm-thick polished plates cut from glasses prepared by a conventional technique of melting the initial oxides in platinum or ceramic crucibles. The composition of the initial components loaded into the crucibles and that of the samples analyzed with an x-ray microanalyzer (JEOL) are listed in Table 1.

Raman spectra were measured on a triple Raman spectrograph with a macrochamber in a scattering configuration at a 90° angle. An argon laser was used at the 514.5-nm wavelength as exciting radiation. The reduced Raman spectra (being the closest in the form of their spectral dependence to SRS spectra) were calculated from the experimental spectra by multiplication by a factor of $1/(1+n_b)$, where n_b is the Bose-Einstein factor $n_b = [\exp(hc\omega_R/kT)]^{-1}$.

We used the Raman spectrum of the silica glass KU-1 as a reference, thus taking the most intensive Raman band at 440 cm⁻¹ (VV polarization) as unity. The reduced spectra were additionally multiplied by a factor F that takes into account the changes in scattering geometry and their intensity related to the refractive-index value of the samples. Since different values of this factor are used in various papers,^{6–9} it is possible to give the expressions for all its constituents here. In all investigated glasses the radiation

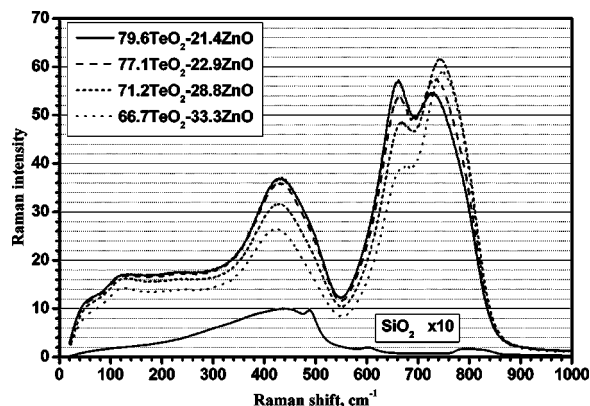


Fig. 1. Reduced Raman spectra (VV polarization) of a glass system $x\text{ZnO}-(100-x)\text{TeO}_2$.

Table 1. Composition, Factor F , and Raman Band Intensities of the Investigated Glasses

Charge Composition, (mol. %)	Analysis Results (JEOL)	Factor F	Ratio of Intensities of the Raman Band and the 440-cm ⁻¹ band in SiO ₂		
			460 cm ⁻¹	650–750 cm ⁻¹	900–920 cm ⁻¹
10 WO ₃ –90 TeO ₂	12.5 WO ₃ –87.5 TeO ₂	2.82	50	90 (668)	45
15 WO ₃ –85 TeO ₂	14.8 WO ₃ –85.2 TeO ₂	2.79	47	90 (668)	52
20 WO ₃ –80 TeO ₂	18.9 WO ₃ –81.1 TeO ₂	2.73	45	85 (672)	58
25 WO ₃ –75 TeO ₂	24.8 WO ₃ –75.2 TeO ₂	2.67	40	79 (685)	65
20 ZnO–80 TeO ₂	21.4 ZnO–79.6 TeO ₂	2.45	37	54 (736)	-
25 ZnO–75 TeO ₂	22.9 ZnO–77.1 TeO ₂	2.44	36	58 (738)	-
30 ZnO–70 TeO ₂	28.8 ZnO–71.2 TeO ₂	2.37	32	62 (748)	-
35 ZnO–65 TeO ₂	33.3 ZnO–66.7 TeO ₂	2.27	26.5	59 (752)	-
15 TiO ₂ –85 TeO ₂	13.5 TiO ₂ –86.5 TeO ₂	2.41	45	60 (660)	-
10 GeO ₂ –90 TeO ₂	10.9 GeO ₂ –89.1 TeO ₂	2.45	50	80 (665)	-
17 MoO ₃ –18 WO ₃ –65 TeO ₂	16.7 MoO ₃ –19.6 WO ₃ –63.7 TeO ₂	2.64	38	75 (720)	96
14 Sb ₂ O ₃ –86 TeO ₂	2.1 WO ₃ –19.1 Sb ₂ O ₃ –78.8 TeO ₂	2.30	44	46 (665)	20
30 MoO ₃ –70 TeO ₂	29.0 MoO ₃ –71.0 TeO ₂	2.95	35	63 (740)	95

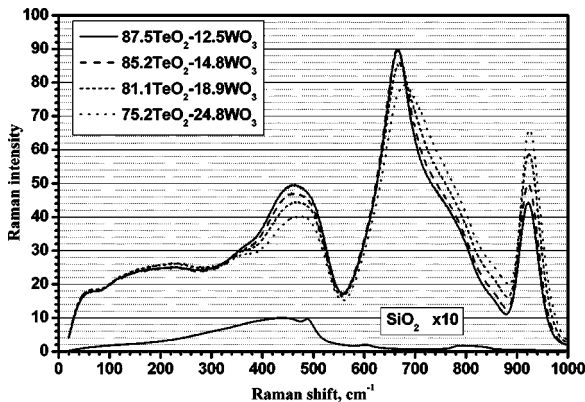


Fig. 2. Reduced Raman spectra (VV polarization) of a glass system $x\text{WO}_3-(100-x)\text{TeO}_2$.

absorption was considered to be weak enough, and hence it was not taken into account.

Factor F can be broken into four factors: $F = F_L F_C F_{\text{out}} F_V$, where the first factor, $F_L = (1 - R_{\text{SiO}_2}^2) / (1 - R_{\text{TeO}_2}^2)$, takes into account the difference in exciting radiation power inside the samples at its constant input value for each sample, and $R = (1 - n)^2 / (1 + n)^2$. The second factor, $F_C = n_{\text{TeO}_2}^2 / n_{\text{SiO}_2}^2$, allows for the difference in a solid angle of radiation falling into the spectrometer and scattered from the samples, with equal thickness and various refractive-index values n . The third factor, $F_{\text{out}} = (1 - R_{\text{SiO}_2}) / (1 - R_{\text{TeO}_2})$, accounts for the reflection of radiation scattered from the surface, through which this radiation is collected in the spectrometer. At a 90° scattering geometry and for samples with small thickness the last factor (which depends on the scattering volume) is $F_V = 1$.

Raman spectra for VV polarization of a glass system $x\text{ZnO}-(100-x)\text{TeO}_2$ (where x ranges from 21.4 to 33.3 mol. %) are shown in Fig. 1. As the zinc oxide concentration increases, one can see the following

changes in the spectra: a strong decrease in the 450- and 660-cm⁻¹ band intensities (disproportionate to the decrease in the tellurium oxide concentration), growth of the highest-frequency band, and its shift from 730 to 750 cm⁻¹. The relation between the vibration spectra of this glass system and its structure was discussed in Refs. 10–12. Note that for a zinc oxide concentration of approximately 20 mol. % the intensities of the 660- and 750-cm⁻¹ bands become equal and the peak of their total band appears to be mostly flat.

Raman spectra for VV polarization of a glass system $x\text{WO}_3-(100-x)\text{TeO}_2$ (where x varies from 12.5 to 24.8 mol. %) are presented in Fig. 2. The intensity of a wide Raman band with a shift at 600–800 cm⁻¹ is 80–90 times the value for the reference SiO₂ glass. As the tungsten concentration increases, a transformation of the Raman spectra occurs: The peak intensity decreases slightly, and it widens because of high-frequency wing growth; a drop in 450-cm⁻¹-band intensity is observed, as well as the growth of the 920-cm⁻¹ band typical for WO₃ and its small shift by 5 to 925 cm⁻¹. The relation of the Raman spectra to the structure of such glasses was analyzed in Ref. 13. Glasses of this system are the most stable tellurite glasses. They allow the introduction of up to 10 mol. % of rare-earth elements and have, as is obvious from Figs. 1 and 2, more intensive Raman spectra than the $x\text{ZnO}-(100-x)\text{TeO}_2$ system. Measurements of Raman scattering cross sections for glasses of the system $x\text{WO}_3-(100-x)\text{TeO}_2$ in backscattering geometry with the use of a confocal microscope were used in Ref. 9. The gain coefficient values calculated from the Raman spectra measured in that work are twice as high as those measured in Ref. 5 and 20% higher than those obtained from our measurements. Since the authors of Ref. 5 did not say whether they took factor F_C into account and the authors of Ref. 9 said nothing about factor F_V and the polarization of the

scattering spectra, it is impossible to determine whether our measurements or those of Refs. 5 or 9 are more accurate.

Figures 3 and 4 show the reduced Raman spectra for some other tellurite glass compositions. Frequencies of the Raman bands, their intensities, and factor F for the glass compositions studied in our Letter are listed in Table 1.

In our opinion, tellurite glasses containing MoO_3 are of special interest for the development of Raman amplifiers. Raman spectra and their relation to the structure of MoO_3 - TeO_2 glasses were investigated in Ref. 14. However, the comparisons of MoO_3 - TeO_2 Raman band intensities with those for SiO_2 or for other compositions of tellurite glass are absent in this work.

As is seen from the figures and the table, the intensity of the fundamental bands in the Raman spectra of tellurite glasses is 20–95 times higher than that in silica glass. The total Raman bandwidth and frequency shifts, which can be achieved in fiber Raman amplifiers operating with tellurite glasses, are also much greater than those in silica glass. We also point out the presence of a highest-frequency Raman band with a shift of more than 900 cm^{-1} , which exceeds the Raman band intensity in silica glass by 50–90 times

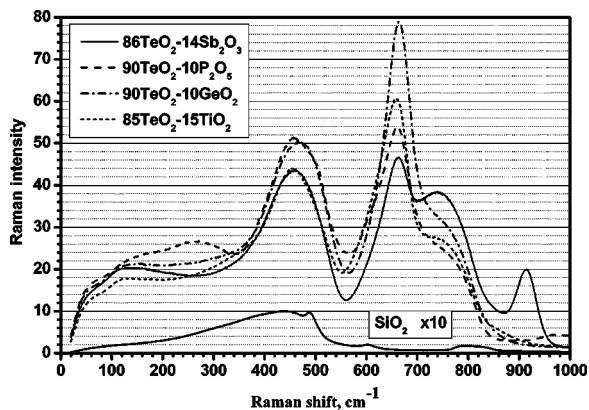


Fig. 3. Reduced Raman spectra (VV polarization) of Sb_2O_3 - TeO_2 , P_2O_5 - TeO_2 , GeO_2 - TeO_2 , and TiO_2 - TeO_2 glasses.

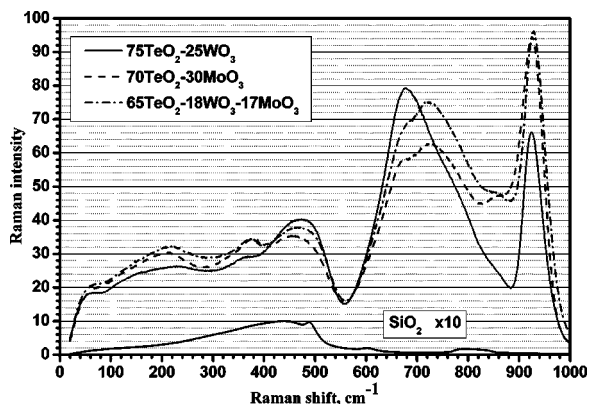


Fig. 4. Reduced Raman spectra (VV polarization) of WO_3 - TeO_2 , MoO_3 - TeO_2 , and MoO_3 - WO_3 - TeO_2 glasses.

for the WO_3 - TeO_2 glass system and by 95 times for the MoO_3 - TeO_2 glass system. It is shown for the first time to our knowledge that MoO_3 - TeO_2 and MoO_3 - WO_3 - TeO_2 glass systems can be considered the most prospective fiber material for the development of SRS amplifiers.

A few methods of Raman gain bandwidth flattening have been developed, among which the use of long-period intrafiber-lattice¹⁵ cutting peaks on a gain curve or the application of spectrally broadened fiber Raman amplifiers¹⁶ and multiline pumping¹⁷ can be considered the most simple and effective. Fitting the pump wavelength for tellurite glass fibers, it is possible to obtain the Raman amplification with a band from 90 (near $1\text{-}\mu\text{m}$ pumping) to 250 nm (near $1.55\text{-}\mu\text{m}$ pumping) at a tenfold excess of the signal gain as compared with silica-based fibers in any of the regions (S, C, L, \dots), which is of interest for fiber-optic communication.

V. G. Plotnichenko's email address is victor@fo.gpi.ac.ru

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