Raman Gain in Tellurite Glass: How Combination of IR, Raman, Hyper-Raman and Hyper-Rayleigh Brings New Understandings

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S *Supporting Information*

ABSTRACT: A new multimodal approach that combines linear and nonlinear vibrational spectroscopies and hyper-Rayleigh scattering has been applied in the $TeO_2-TaO_{5/2}-ZnO$ glass system to assess and quantify the relation between Raman gain and optical responses within the glass' network arrangement. The level of polymerization of the TeO_4 chain-like structure in a TeO_2 glass system has been identified to be the main parameter for reaching high linear and nonlinear optical constant. We have observed that replacement of $TaO_{5/2}$ by ZnO strongly modifies the optical properties and, primarily, the Raman and hyper-Raman spectra of the glasses. In particular, we clearly demonstrate a linear relationship between Raman gain and the linear and second-order optical response of the glass, which is directly related to the number density of TeO_4 chain-like units. Assuming that only TeO_4 chain-like units contribute significantly to the glass' polarizability, we have found that about 30% of the Te atoms contribute to the hyperpolarizability of the binary system $80TeO_2-20ZnO$ in very good accordance with neutron diffraction results.
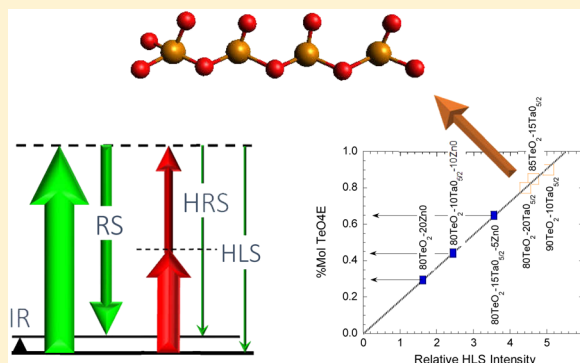
INTRODUCTION

Stimulated Raman scattering (SRS) is a nonlinear optical phenomenon (third-order susceptibility) widely investigated because it offers an unique alternative to rare earth containing materials for numerous applications in telecommunication and more generally in optoelectronic components such as amplifiers and fiber lasers. Thanks to the generation of gain by the stimulated emission of a photon at a frequency that is down-shifted by the vibrational modes of a medium, the SRS effect can span a broad range of the spectrum available. Devices based on the Raman gain process bring important agility to optical components since the gain can be obtained on a wide frequency domain as the mechanism depends only on the vibration mode of the materials and the selected line of the pumping laser. Heavy metal oxide (HMO) glasses are excellent candidates for such purpose due to their broad spectral transparency and the attributes of their high atomic mass constituents. Over the past 20 years, significant effort has been made in numerous glass systems to relate the glass' structure to the Raman response of such materials. Among those HMO materials, tellurite glasses occupy an unique position which combines a high linear and nonlinear response, with wide optical transparency and good chemical stability.

Stegeman et al. have demonstrated that spontaneous Raman cross-section measurement can be used for estimating the Raman gain response of the different glass samples if precautions are taken for calibration.[1] The relative Raman gain coefficient, normalized to SiO_2, can then be retrieved while taking into account any possible resonance effects through careful choice of the excitation wavelength.[2] It has been clearly shown that the Raman response is driven by the tellurium oxide network former's response within the multicomponent glass network, but the influence of the other constituents of the glass are decisive for monitoring the magnitude of the response. The effect of introduction of various metal oxides in tellurite glass has been investigated by various research groups. Here, the d^0 transition ions such as Ti^{4+}, Nb^{5+}, or W^{6+} have been identified to favor high Raman gain coefficient.[3−5] It remains that the understanding of the relation between optical response and its

structure is challenging and a new approach is necessary beyond the complex measurement tools employed in the prior efforts, which offers a direct link between the glass network structure and the resulting nonlinear optical properties.

Scheme 1. Energy Diagram and Multipolar Activity for Infrared (IR) Absorption, Raman (RS), Hyper-Raman (HRS), and Harmonic Light (HLS) Scattering in Isotropic Materials Following Reference 11
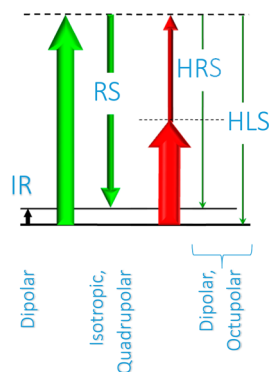
To date, general tendencies have been established between the evolution of electronic nonlinear properties and the chemical constituents within structural entities without being able to *directly relate* dedicated types of network structural features to the observed optical activity. The existence of the lone pair of electron on the tellurium has been proposed to be a primary factor for promoting the high polarizability and hyperpolarizability.[6,7] It remains that the estimation of the

electronic response leading to the third-order polarizability (also called second-order hyperpolarizability) is not an easy task. Different approaches have been conducted and have led to the conclusion that small clusters do not represent properly the glass network's nonlinear optical response.[8] It appears that a high second-order hyperpolarizability is not simply related to the local electronic response but also to the chain-like structure of the tellurite network engaging Te−O−Te bonds.[9] Regarding the specific case of the stimulated Raman scattering, no such theoretical approach has to date, been conducted.

In this work, $TeO_2−TaO_{5/2}$-ZnO glasses have been fully investigated to understand the relationship between the glass network's skeleton structural entities and the linear and nonlinear optical responses. In a previous work,[10] we have presented preliminary results on this glass system where we have shown that there is a direct correlation between the Raman gain efficiency and the structure of tellurite glasses and that deeper studies including new experimental methodologies are necessary. This work presents a discussion of these additional methodologies.

Here, we will apply a new multimodal approach which has been recently introduced[11] and where we combine linear and nonlinear vibrational spectroscopies (depicted in Scheme 1) that allows one to bridge the gap previously described. It is known that infrared (IR), spontaneous Raman (RS), and hyper-Raman (HRS) spectroscopies are powerful tools for investigating matter. They are noninvasive and very sensitive techniques which provide a lot of information at the molecular level. As detailed in a previous work,[11] glasses are isotropic media and light interaction in such media is subject to isotropic averaging of the local symmetry (multipolar activity). In
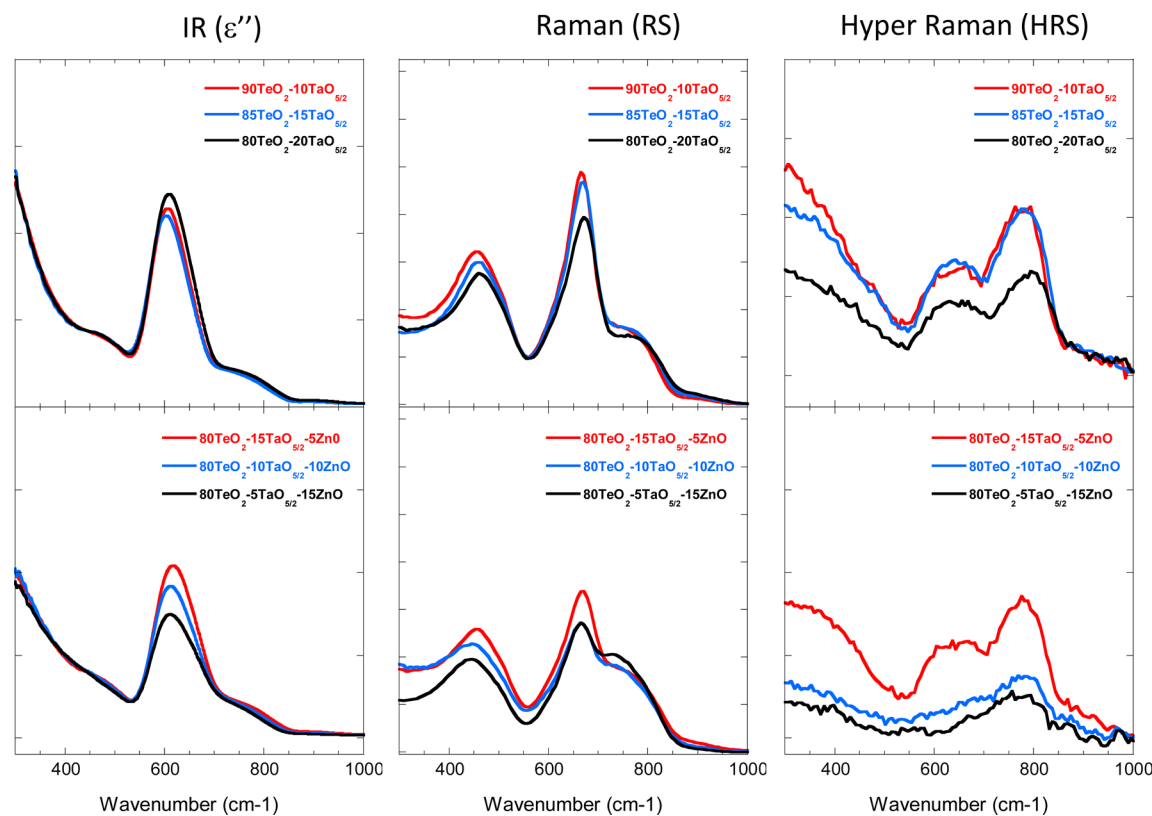

Figure 1. Infrared (ε'') (IR: left), VV polarized Raman (RS: middle) and hyper-Raman (HRS: right) spectra of bulk glasses. The Raman and hyper-Raman intensities are in arbitrary units.

isotropic media, the mutual exclusion rules applies and the even symmetry representations (isotropic and quadrupolar) are Raman active while odd symmetry representations are IR active (dipolar) and HRS active (dipolar and octupolar).

Besides extended vibrational studies which basically provide structural and dynamical information at a short-range scale in glasses, a good knowledge of the whole electronic polarizability of the material is necessary to obtain a more complete understanding of structure/properties relationships for photonic applications. Following this, it is of importance to look at the inter-relationship between the linear and nonlinear dielectric susceptibilities—up to the third-order—which are the bulk key properties in light-matter interaction. Bulk linear susceptibilities will be quantified from the index of refraction of the glasses which are determined by measuring the p-polarized reflectivity of the samples around the Brewster angle as described elsewhere.[12] The second-order susceptibility of material can be measured using hyper-Rayleigh scattering, also called harmonic light scattering (HLS) or second harmonic scattering (SHS). Here, HLS is the elastic counterpart of hyper-Raman, where we detect the scattered light at the optical frequency 2ω from an intense incident laser pulsed at ω (Scheme 1).[13] Through the years, HLS has become a popular and well adapted technique to quantify hyperpolarizability of molecules.[14] HLS is also a powerful selective method for characterizing nanoparticles and macroparticles[15−17] and we have recently shown that polarization-resolved HLS is a unique tool to probe complex multipolar (dipolar and octupolar) symmetry structures of elementary structural units (ESU) in isotropic materials, like ionic liquids,[18] and even silica glass.[11] As demonstrated by Stegeman et al.,[1] the measurement of the Raman cross section provides—in addition to structural information—relevant information on the magnitude of the third order-susceptibility assigned to the different structural items. We exploit this inter-relationship in our efforts to assign optical response to specific structural entities within the multicomponent tellurite glass system examined here.

The paper is organized as follows. In the Results, we start by presenting an extended vibrational study, using IR and polarized-resolved Raman and hyper-Raman spectroscopies, and by interpreting the glass spectra using a unified desummation of the vibrational peaks. Then, the experimental investigations of the second-order susceptibilities on the complete set of glass composition are reported and discussed. Finally the last section (Discussion) contains an overall discussion where both the vibrational results and susceptibilities responses are considered and correlated to draw concluding remarks about structure-properties relationships in the $TeO_2-TaO_{5/2}-ZnO$ glass system.

RESULTS

Extended Vibrational Studies: Unified Analysis of the Vibrational Bands. The IR, Raman and hyper Raman spectra of the glass system $(100 - x)TeO_2 - (x - y)TaO_{5/2} - yZnO$ are reported in Figure 1. Whatever the change in composition between the network former TeO_2, the intermediate $TaO_{5/2}$, and the modifier species ZnO, we observe in Figure 1 that each vibrational technique gives more or less the same spectral shape but differences in the intensity of some bands can be better found in Raman spectra and even more in hyper-Raman spectra. This first observation indicates that the addition of tantalum and even its substitution with zinc do not drastically change the basic structure of the tellurite network.

The attribution of the different vibrations bands observed in Raman and infrared spectroscopies have been discussed earlier.[10] A unified desummation of the spectra has been conducted (see Table 1) using eight modes including their

Table 1. Summary of the Spectral Desummation for IR, Raman, and Hyper-Raman Spectra Using Normalized Gaussian Function for Three Selected $TeO_2-TaO_{5/2}-ZnO$ Glass Compositions[a]

| Mode assignment | 90TeO₂10TaO₅/₂ | | | | | 80TeO₂20TaO₅/₂ | | | | | 80TeO₂5TaO₅/₂15ZnO | | | | |
	Band position (cm⁻¹)	HWHM (cm⁻¹)	IR	RS (VV)	HRS (VV)	Band position (cm⁻¹)	HWHM (cm⁻¹)	IR	RS (VV)	HRS	Band position (cm⁻¹)	HWHM (cm⁻¹)	IR	RS (VV)	HRS (VV)
1 $\delta_{as}(TeO_4)$	367 66		0.17	0.09	0.21	381 67		0.16	0.12	0.20	386 57		0.18	0.09	0.22
2 $\delta_s(TeO_4)$	465 81		0.24	0.37	0.18	474 74		0.20	0.32	0.14	462 78		0.24	0.31	0.09
3 $\nu_{as}(TeO_4)$	612 41		0.31	0.10	0.10	622 44		0.30	0.13	0.11	607 42		0.28	0.09	0.01
4 $\nu_s(TeO_4)$	666 35		0.09	0.25	0.09	674 36		0.07	0.21	0.08	663 40		0.14	0.20	0.09
5 $\nu_s(TeO_{3+1})$	733 40		0.06	0.09	0.14	746 48		0.07	0.10	0.14	730 51		0.09	0.18	0.21
6 $\nu_{as}(TeO_{3+1})$	791 40		0.03	0.07	0.17	806 42		0.02	0.06	0.14	787 51		0.03	0.12	0.30
7 TaO_n	870 102		0.03	0.02	0.08	870 121		0.04	0.04	0.14	870 67		0.02	0.01	0.04
8 TaO_n ?	574 36		0.08	0.00	0.03	584 39		0.14	0.01	0.04	562 36		0.03	0.00	0.04

[a]All of the intensities have been normalized to the total spectral density.

assignment, as shown for the glass composition $90TeO_2-10Ta_2O_5$ (binary system) in Figure 2 and $80TeO_2-5TaO_{5/2}-15ZnO$ (ternary system) in Figure 3. Although Table 1 refers only to VV polarized (Raman and hyper-Raman) results for clarity and concision purpose, note that we have reported all the HV spectra in Figures 2 and 3 to demonstrate the relevance of the desummation we performed using these three vibrational techniques. For those optical spectroscopies, the tellurium oxide structural units constitute the primary (strong bands) contribution to the spectra. Weak bands can be attributed to tantalum based structural units. In the different spectra, the sharp modes 3 and 4 picking around 610 cm⁻¹ (mainly IR active) and 660 cm⁻¹ (mainly Raman active) are attributed respectively to antisymmetric and symmetric stretching of TeO_4 units in tellurite chain-like structure. These units are trigonal bipyramidal disphenoids which are interconnected through highly asymmetric bridges $O_{axial}-Te-O_{equatorial}$ in the α and β crystalline phases of TeO_2. The symmetric mode 4 at around 660 cm⁻¹ dominates the Raman spectrum whereas its intensity is weaker in the HRS (and also IR) spectrum, indicating in term of multipolar contribution, respectively, a strong isotropic activity but a weaker dipolar activity of that band. The modes 5 and 6 at around 730 and 790 cm⁻¹ are assigned respectively to symmetric and antisymmetric stretching of TeO_{3+1} units which are distorted disphenoids with one long Te−O bond.[19] These modes have a moderate intensity in IR and Raman whereas they contribute strongly to the HRS spectral density. Note that, based on *ab initio* molecular-dynamics simulations, Pietrucci et al. attributed those vibrations to strongly localized vibrational modes of units with oxygen bridging the tellurium and another metal ions Te−O−M.[20] Modes 1 and 2 at around 370 and 465 cm⁻¹ correspond respectively to antisymmetric and symmetric -highly coupled-
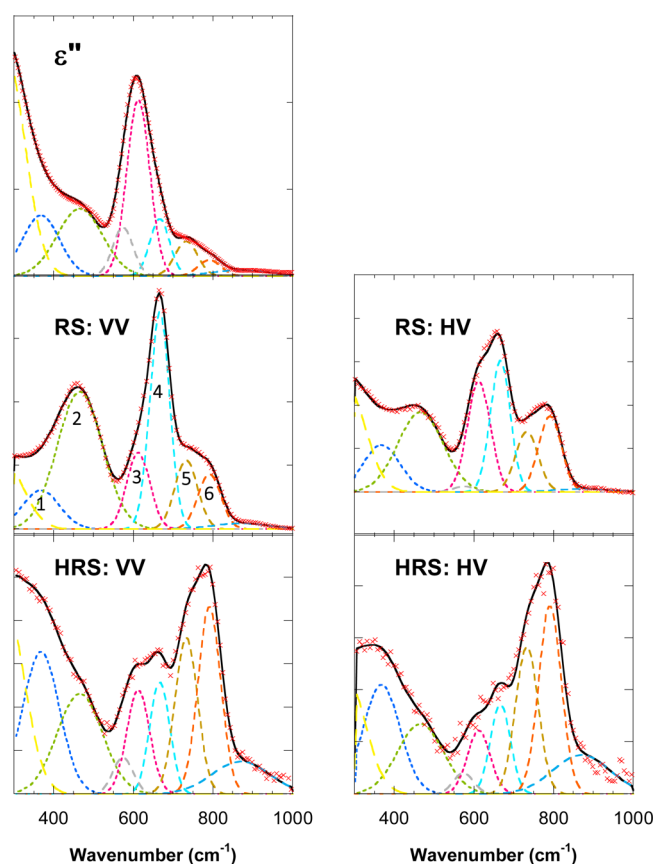
Figure 2. Infrared (top), Raman (middle) and hyper-Raman (bottom) spectra of $90TeO_2 10TaO_{5/2}$.

Figure 3. Infrared (ε'') (top), Raman (middle) and hyper-Raman (bottom) spectra of $80TeO_2-5TaO_{5/2}-15ZnO$.

stretching-bending modes of continuous Te−O−Te chains with corner sharing TeO_4 polyhedra. The symmetric bending mode 2 clearly dominates the RS spectrum whereas the asymmetric mode 1 is more intense in the HRS spectrum. In term of multipolar activity, the symmetric bending mode 2 is mostly isotropic/quadrupolar and exhibit a poor dipolar contribution whereas the corresponding antisymmetric bending mode 2 is much more dipolar since it dominates the HRS spectrum. Note that RS and HRS intensities in the Stokes low frequency range (typically below 400 cm^{-1}) are temperature enhanced because we did not apply the temperature correction (Bose−Einstein population factor). As a consequence, the low frequency half-band (color: yellow) is not considered since it has just been "technically" introduced in this procedure to fit properly the eight bands reported in Table 1 and actually discussed. Lastly, very weak TaO_6 vibrational contributions (stretching mode) are also expected at 870 cm^{-1} as reported by Wada[21] and presumably here around 570−580 cm^{-1}.

The evolution of the normalized intensities are composition- and spectroscopy-dependent. In the tantalum tellurite glass $90TeO_2$-$10TaO_{5/2}$ (Figure 2), the IR and RS spectra are dominated by the TeO_4 disphenoids contribution (modes 3 and 4) while in the HRS spectra, the contribution of the modes associated with TeO_4 and TeO_{3+1} remains comparable. In the ternary glass $80TeO_2−5TaO_{5/2}−5ZnO$ where zinc oxide has been introduced (Figure 3), slight differences are observed in the VV and HV RS spectra that are more pronounced in the VV and HV HRS spectra. Notably, HRS intensity of the Te−O−Te chain structure (mode 2) decreases of about 50% (VV), the HRS intensity of the asymmetric stretching (mode 3) of the
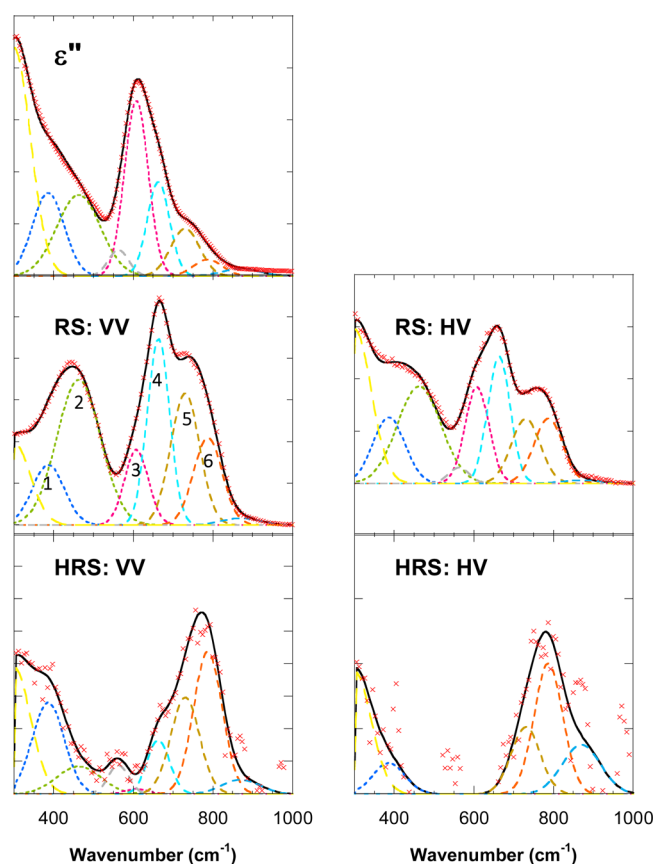
TeO_4 units almost disappears. At the opposite, the modes associated with the TeO_{3+1} units (5 and 6) are clearly visible in the HRS VV and HV spectra (Figure 3).

Structural Insights from Harmonic Light Scattering. HLS polarization and power scans have been recorded to quantify the second-order response of the glasses, following the procedure described in Supporting Information. Acetonitrile has been used as an external reference.[13] Typical power and polarization scan curves obtained with $90TeO_2−10TaO_{5/2}$ are reported in Figure S2 and results are gathered in Table S1, including previous data obtained for vitreous SiO_2 (v-SiO_2) for comparison and normalization purposes.[11] When the tantalum oxide is introduced in TeO_2, the amplitude β_{HLS}, which depends on the spatial extent of the ESU, decreases slightly while the anisotropic parameter r_{ap} (octupolar to dipolar ratio), which is a structural indicator, holds around 1.1, which is approximately expected for an ESU based on a TeO_4 asymmetric structural unit.[22] As soon as the zinc oxide is introduced to replace tantalum, β_{HLS} drops drastically down to nearly half of its highest value while the anisotropic parameter r_{ap} still holds around 1.1, within the experimental errors. The introduction of zinc oxide clearly triggers a decrease of the amplitude of the hyperpolarizability of the Te-based ESUs while the symmetry of the HLS-active basic unit is unchanged. Such evolution cannot be only composition related but has to be associated with a major structural change of the tellurium oxide glass network, the backbone of the glass. The impact of the introduction of zinc oxide in the ternary system can be also detected on the linear optical properties with a decrease of the refractive index of the material (Table S1). Before this point will be discussed in

a more general context in the last section, let us focus first on the second-order response. Figure 4 reports the evolution of the HLS intensity normalized to silica v-SiO$_2$ with the Te atomic content since the Te network contributes almost totally to the optical susceptibilities.

For the binary Te−Ta system, we observe direct linear behavior of the second-order intensity which is typical of a HLS incoherent scheme where the intensity of each ESU (scatterer) adds linearly. This observation suggests that the ESU, the TeO$_4$ chain-like based unit, remains unchanged but is simply "diluted" as the tantalum content increases. This result is perfectly in accordance with a previous hyper-Raman and Raman study of paratellurite α-TeO$_2$ crystal that we performed and where we concluded it was instead classified as a molecular crystal rather than a framework-like network.[23] In the case of a framework-like glass network, the second-order intensity is expected to deviate from linearity when modifying the glass composition because the ESUs contributing to the HLS responses are expected to be modified structurally involving experimental changes in volume, symmetry, etc.. In the ternary system, strong modifications are experienced by the glass network. One major point is the relative decrease of density of the material with zinc oxide addition (see Table S1 in Supporting Information). It gives rise to a relative slight increase of the Te content accompanied by a drastic (however linear) decrease of the second-order response (see Figure 4). Clearly here we see the effect of zinc oxide that strongly modifies the glass network (glass modifier): this can simply be interpreted as a linear decrease of the number of TeO$_4$ chain-like units which affects strongly the second-order susceptibility because previous ESUs which have been modified in structure/length do not contribute any more to the HLS intensity. Here we observe a typical behavior of what we could call a "molecular-like glass".
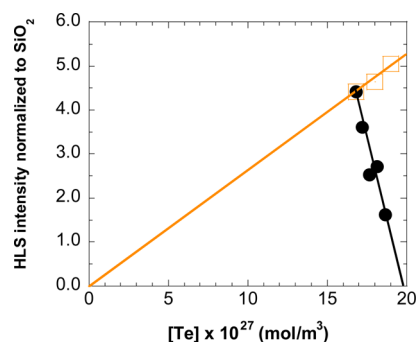

Figure 4. Normalized HLS intensity ($|\beta_{HLS}|^2$) as a function of Te atomic content for the binary Te−Ta system (empty square) and the ternary Te−Ta−Zn system (full circle).

■ DISCUSSION

Table 2 reports a summary of the linear and nonlinear susceptibility intensities relative to v-SiO$_2$. Whatever the order of the optical response, we can see from Table 2 that all the intensities are sensitive to the introduction of tantalum and even more impacted by zinc which drastically perturbates the optical susceptibility. The effect of the introduction of zinc oxide is clearly not solely due to a composition variation but must be related to a global change of the polarizability nature of the glass network. Since no concurrent (nor significant) absorption change is occurring, a modification due to a

Table 2. Te Atomic Content, First-Order Intensity (at 1064 nm), HLS Intensity $|\beta_{HLS}|^2$ (at 1064 nm), and Raman Gain (at 752 nm) Relative to SiO$_2$^{a}

	[Te] $\times 10^{27}$ mol/m^3	Relative First-order intensity* $|\chi^{(1)}|^2$	Relative HLS intensity	Relative Raman gain[#] measured at 660 cm^{-1}
90TeO$_2$-10TaO$_{5/2}$	19.0	57.0	4.1	37.0
85TeO$_2$-15TaO$_{5/2}$	17.9	57.0	3.8	38.0
80TeO$_2$-20TaO$_{5/2}$	16.8	55.5	3.6	31.0
80TeO$_2$-15TaO$_{5/2}$-5ZnO	17.2	52.5	3.0	27.5
80TeO$_2$-10TaO$_{5/2}$-10ZnO	17.6	47.0	2.1	23.0
80TeO$_2$-5TaO$_{5/2}$-15ZnO	18.1	44.4	2.2	18.0
80TeO$_2$-20ZnO	18.6	40.7	1.3	-

^{a}Key: (∗) The first-order intensity at 1064 nm is given by $|\chi^{(1)}|^2 = [(n^2 - 1)/4\pi]^2$ where n is the index of refraction at 1064 nm given in Table S1 (Supporting Information). (#) Values reported from ref 10.

resonance effect cannot be proposed either. The origin of the phenomenon must rely in the glass network's organization.

These changes are better visualized in Figure 5 (left) which summarizes all susceptibilities but also vibrational modes behavior associated with Te content. Clearly, Figure 5 highlights a strong linear correlation between the optical intensities, whatever the order of the response (linear, second and third order nonlinear responses), when changing the glass composition.

In the tantalum tellurite (TT) binary system, according to the IR, Raman and hyper-Raman spectroscopies (Figure 5: middle and right), neither modes 3 and 4 from TeO$_4$ units nor modes 5 and 6 from TeO$_{3+1}$ exhibit a large intensity change, indicating that the tellurite network is weakly affected by the variation of the tantalum content. Here both the vibrational results and optical susceptibilities responses follow the same trend: we observe that in the binary glass system TeO$_2$−TaO$_{5/2}$ the introduction of octahedra [TaO$_6$] modifies in a moderate way the TeO$_4$ chain-like structure, reducing partially the polarizability but within the experimental errors no clear change happens in the IR, RS and HRS vibrational spectra.

In contrast, in the zinc tantalum tellurite (TTZ) ternary system, the response of the TeO$_4$ (modes 3 and 4) is seen to rapidly decrease in the Raman and the hyper-Raman spectroscopies when the zinc oxide content increases. As evoked by HLS results, this effect is related to a change in the TeO$_4$ chain-like structure due to the disappearance of the Te−O−Te bridges and the formation of Te−O−Zn bonds, leading to an increase of distorted TeO$_{3+1}$, i.e. an increase of mode 5 and 6 intensity. This balance effect between the disappearance of modes 3 and 4 versus the appearance of mode 5 and 6 is well pronounced in the Raman and hyper-Raman spectra but not observed in the IR response where modes 3 and 4 seem to increase with zinc addition. However, the intensity differences observed upon the considered technique are expected and fully consistent since both Raman and hyper Raman responses are directly connected to the electronic contribution (polarizability/susceptibility) of the ESU whereas this is not the case of the IR spectroscopy which is more sensible to structural changes. For example, for 20% of ZnO introduced, the normalized hyper-Raman intensity of TeO$_4$ modes 3 and 4 becomes weak and hardly distinguishable (less than 0.1 in Figure 5). This is not the case for the IR spectrum, where
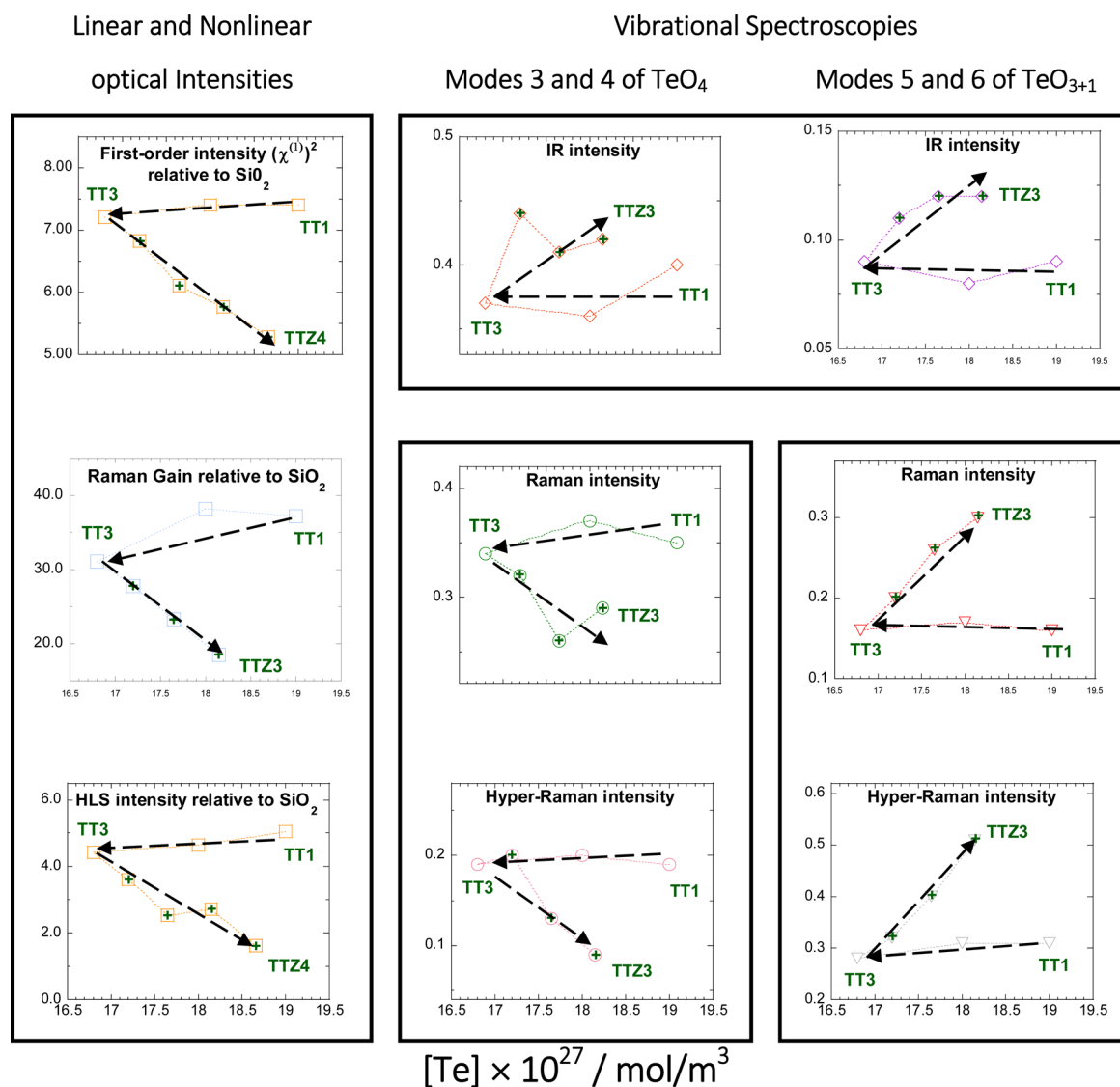
Figure 5. Left: Linear (first-order) and nonlinear (Raman gain and HLS) intensities normalized to v-SiO$_2$. IR, RS (VV), and HRS (VV) intensities (normalized to the total spectral density) of modes 3 and 4 from TeO$_4$ (middle) and of modes 5 and 6 from TeO$_{3+1}$ (right). TT1 (90TeO$_2$-10TaO$_{5/2}$), TT3 (80TeO$_2$-20TaO$_{5/2}$), TTZ3 (80TeO$_2$-5TaO$_{5/2}$-15ZnO), and TTZ4 (80TeO$_2$-20ZnO) defines border compositions (TTZ data, i.e., the Te−Ta−Zn system, are highlighted with crosses). Arrows are guides for the eye.

modes 3 and 4 have a strong IR intensity (*ca* 0.4 in Figure 5) although their IR intensity change with ZnO addition is less clear.

Undoubtedly, the introduction of ZnO in the glass matrix leads to a decrease of the Raman cross section of the TeO$_4$ molecular entities (primarily responsible for the Raman gain), reinforcing the hypothesis that the ZnO changes the network layout and breaks the TeO$_n$ chain-like which are at the origin of the strong (hyper)polarizability by forming ZnO$_{4+1+1}$ units as proposed by Kozhukharov et al.[24] An *ab initio* approach developed by Mirgorodsky et al. has led to the conclusion that such observations could result from a "manifestation of nonlocal effects in the electronic distribution response" and that the chain like structure length remains the factor governing the hyperpolarizability.[9] If so, a disruption of those chains will strongly affect the resulting polarizability of the glass network. This effect can be related to the decrease of the size and the efficiency of the scattering. When the ZnO is introduced in large concentration, the tellurite chains forming the glass

network rearrange to form shorter units corresponding more to an "isolated" TeO$_4$ disphenoid with much lower polarizability and hyperpolarizability. The drastic linear decrease of the second-order intensity reported in Figure 4 (and Figure 5) is in agreement with this. Results from extended vibrational spectroscopy clearly indicate the strong correlation of the Raman gain evolution and the local structure of the glass with the existence and proportion of chains of TeO$_4$ disphenoids. This structural sequence most likely leads to electronic partial delocalization along the chain which contributes to an overall increase of the polarizability and the hyperpolarizability as compared to isolated units. Note however that the balance between the odd ($\chi^{(1)}$, $\chi^{(3)}$...) and even ($\chi^{(2)}$...) contributions of the total polarizability of the ESU is entirely symmetry dependent.

Kozhukharov et al. performed a neutron diffraction study of a zinc-tellurite glass with composition 80TeO$_2$−20ZnO.[24] In this study, they concluded that approximately 35% of the Te atoms conserve the same coordination state as in the α-TeO$_2$ crystal

structure, i.e., the TeO_4 chain-like structure. Figure 6 highlights different HLS results from Figure 4 by reporting the relative molar content of TeO_4 units as a function of the experimental HLS intensity. It means that we assume for the ternary system Te−Ta−Zn that only the residual TeO_4 chain-like ESUs do contribute significantly to the glass polarizability. Under this simple hypothesis, the HLS results indicate that about 30% of the Te atoms conserve the same coordination state as in the α-TeO_2 crystal structure for the binary system 80TeO_2-20ZnO. This is in excellent accordance with neutron diffraction results from Kozhukharov et al.
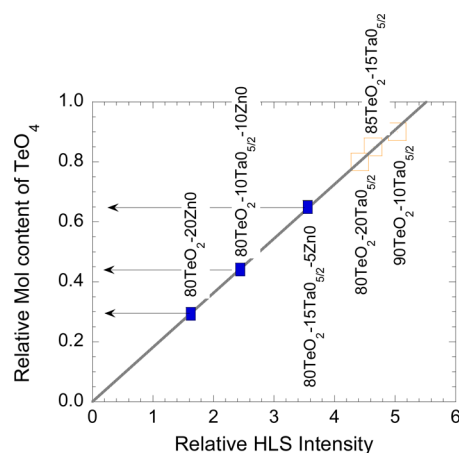

Figure 6. Relative molar content of TeO_4 trigonal bipyramidal units as a function of the relative HLS intensity normalized to SiO_2.

CONCLUSION

The relationship between the tellurite glass composition, its structure, and the optical polarizability and hyperpolarizability is challenging to understand, while the impact of such understanding can be significant in efforts to create novel photonic materials. A combination of linear and nonlinear vibrational spectroscopies and hyper-Rayleigh scattering have been applied to establish this relation in well-chosen glass matrices. The level of polymerization of the TeO_4 chain-like structure in a TeO_2 glass system has been identified to be the main parameter for reaching high linear and nonlinear optical constant. The introduction of zinc oxide in the tellurite glass network, while disrupting the Te−O−Te chain-like structure, leads to a decrease of the magnitude of those constants. A linear relationship between Raman gain, hyperpolarizability intensity, and even linear optical polarizability has been established. This complete vibrational approach turns out to be very effective and promising for the investigation of the structure property relationship in glass and, in particular, the identification of the relevant structural entities responsible for the optical response of the tellurium oxide glass network.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b07627.

> Experimental details about IR, Raman, hyper-Raman, and polarized-resolved harmonic light scattering, and detailed results obtained from harmonic light scattering studies of each glass composition (PDF)

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Notes

The authors declare no competing financial interest.

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