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Raman Scattering Study on Vibrational Modes and Structure of Lanthanum Tellurite Glasses

Angelos G. Kalampounias*  
Department of Chemical Engineering, University of Patras and Institute of Chemical Engineering and High Temperature Chemical Processes, FORTH/ICE-HT, P.O. Box 1414, Patras, GR-26 504, Greece  
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Raman spectra of \( x \La_2\O_3\(1-x\)\TeO_2 \) \( (x=0, 0.05, 0.10, 0.15, 0.20, \text{ and } 0.25) \) lanthanum tellurite glasses were measured and analyzed over the entire glass-forming region in an effort to quantitatively follow the structural changes caused by lanthanum oxide variation. For the first time, systematic intensity measurements have been performed to elucidate the composition induced structural changes in the high-frequency stretching vibration region and a possible mechanism was proposed. The network structure of the glasses is formed by mixing \( \TeO_4 \) trigonal bipyramid and \( \TeO_3 \) trigonal pyramid units. The change of the lanthanum oxide content results in conversion of the \( \TeO_4 \) units to \( \TeO_3 \) units with a varying number of non-bridging oxygen atoms. Analysis of the Raman band contours in terms of vibrations due to different oxygen bridged trigonal bipyramid and trigonal pyramid tellurite structural units, allowed to calculate the relative amounts of the species involved in the structural changes with composition. The fraction of the terminal oxygen atoms has been estimated from the Raman intensities with the aid of a structural model concerning the structure of tellurite network systems. The simulation of the experimental density of lanthanum tellurite glasses with modifier content up to 25% revealed that the short range order building units assumed here are sufficient to account for the overall structure in these glasses.

Key words: Tellurite glass, Raman spectroscopy, Short-range order, Density model

I. INTRODUCTION

Tellurite glasses have scientific and technological interest due to their attractive physical properties such as low melting points, high dielectric constant [1, 2], high refractive index [2], and good infrared transmissivity [3]. Compared with silicate and phosphate glasses, tellurites exhibit relatively higher refractive indices, dielectric constants, and lower phonon energies. The refractive indices allow the utilization of these glasses for non-linear optical materials [4] and the phonon energies have at least two important consequences, the improved infrared transmission up to 6 \( \mu \)m and the low multiphonon decay rates compared to other network oxide glasses. Furthermore, tellurite glasses possess chemical durability and are water resistive [5].

The structure of pure \( \TeO_2 \) and alkali and/or alkaline earth tellurite glasses has been studied with a variety of spectroscopic and diffraction techniques [6–15]. These studies showed, the pure \( \TeO_2 \) trigonal bipyramidal (tpb) structures presented in Fig.1(a), in which one equatorial site of the \( \sp^3d \) hybrid orbitals is occupied by a lone pair of electrons and the other two equatorial and axial sites are occupied by oxygen atoms. The addition of alkali and/or alkaline earth modifiers to pure \( \TeO_2 \) network caused a change in the Te coordination polyhedron from \( \TeO_4 \) tpb to \( \TeO_3 \) trigonal pyramid (tp) in which one of the Te \( \sp^3 \) hybrid orbitals was occupied by a lone pair of electrons [6–15]. The \( \TeO_3 \) tp unit is shown schematically in Fig.1(d). Raman spectroscopy has been proofed as a powerful tool that can elucidate the detailed local structure and provide direct information about the coordination polyhedra being formed in the modified tellurite network.

However, a limited number of works have been focused on the structure of binary glasses containing trivalent modifier, such as second component \( \La_2\O_3 \), while many studies have been conducted on the thermal, elastic and optical properties of binary tellurite glasses containing rare-earth oxides [16, 17].

In this work, we report the room temperature Raman spectra of the \( x\La_2\O_3\(1-x\)\TeO_2 \) \( (x=0, 0.05, 0.10, 0.15, 0.20, \text{ and } 0.25) \) lanthanum tellurite glasses over the entire glass-forming region. The data are discussed in terms of the local structure and the effect of the incorporated cation in the glass-matrix. Emphasis has been given in the analysis of the Raman features and the effect of composition on the structure.
II. EXPERIMENTS

A. Materials

The reagent grade chemicals tellurium(IV) oxide (99.99% purity) and lanthanum oxide (99.95% purity) were purchased from Sigma-Aldrich and used as received. The appropriate amounts of polycrystalline TeO₂ and La₂O₃ were mixed and melted in platinum crucibles at 800–1000 °C for 15–30 min. The homogenized bubble-free liquids were quenched using the conventional method by dipping the crucible into cold water.

B. Measurement

The Raman optical cells were made of silica tubes with the outer diameter of 4 mm, the inside diameter of 3 mm, and 30–40 mm length. About 0.5 g of each \( x \)La₂O₃(1–\( x \))TeO₂ (\( x=0, 0.05, 0.10, 0.15, 0.20, \) and 0.25) glass was transferred into dry, flame and degassed optical cells and finally sealed under vacuum. The cells containing glass powders were heated in vertical tube furnaces above the melting temperature and subsequently quenched to obtain uniform bulk glasses suitable for Raman analysis. In certain cases, heating near the glass transition temperature was adequate for “reverting” the cracks and obtaining defect-free glasses. Thus, the initial stoichiometry of the bulk glass samples did not change after quenching and heat-treatment. The density of glasses was measured using the Archimedes principle. All the weight measurements have an accuracy of ±0.1 mg.

The 441.8 nm line of an air-cooled HeCd laser (Kimmon Electric Co.) was used for the spectra excitation. All room temperature spectra were recorded in a backscattering geometry using a high-resolution UV-Visible Labram HR-800 spectrometer (JY, ISA-Horiba group) under a microscope where the excitation laser beam was focused onto the sample by a microscope objective (50×/0.55). Spectral slit widths (resolution) were set to 2 cm⁻¹, while the scattered light was detected by a CCD detector. Two polarization configurations were used for recording the glass spectra, namely VV (vertical laser excitation-vertical analysis of scattered light) and VH (vertical laser excitation-horizontal analysis of scattered light). A calibration procedure with the aid of a C₆H₆ sample and a Neon lamp took place in order to check the polarization and correct for possible drifts of the monochromator’s gratings, respectively. Accumulation times were adjusted to result in a very high signal-to-noise ratio. Quantitative Raman

FIG. 1 Basic structural polymorphs in TeO₂-based glasses. (a) The TeO₄ trigonal bipyramids (tbp). (b) and (c) The isomeric TeO₅/₂O⁻ units with one non-bridging oxygen atom in equatorial and axial site, respectively. (d) TeO₃ trigonal pyramid (tp) with one neutral non-bridging oxygen atom. (e) The TeO₁/₂O⁻(=O) unit with one charged non-bridging oxygen atom. O⁻ denotes non-bridging oxygen atom. (f) The addition of La₂O₃ into the TeO₄/₂ network leads to the formation of charged TeO₅/₂O⁻-tbp and TeO₁/₂O⁻(=O) tp units with terminal bonds.
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FIG. 2 Stokes-side VV Raman spectra of $x\text{La}_2\text{O}_3-(1-x)\text{TeO}_2$ ($x=0, 0.05, 0.10, 0.15, 0.20$, and $0.25$) glasses at room temperature. The depolarized spectrum (VH) is shown only for pure TeO$_2$ glass. Spectral conditions: excitation line of $441.85$ nm, laser power of $40$ mW, resolution of $2$ cm$^{-1}$, and CCD detector.

Intensity measurements were possible with an error less than $2\%$.

III. RESULTS AND DISCUSSION

Figure 2 shows the room temperature polarized (VV) Raman spectra of $x\text{La}_2\text{O}_3-(1-x)\text{TeO}_2$ glasses with $x=0, 0.05, 0.10, 0.15, 0.20$, and $0.25$. The corresponding (VH) depolarized spectra were measured for all systems but that for pure TeO$_2$ glass is only shown here for clarity. Four bands appear in the high-frequency spectral envelop ($500-850$ cm$^{-1}$) of glasses. These bands are approximately located at $780, 730, 660$, and $610$ cm$^{-1}$.

In the medium frequency range ($400-500$ cm$^{-1}$) two bands located at $\sim 500$ and $\sim 450$ cm$^{-1}$ dominate the spectra at high La$_2$O$_3$ content. These bands are merged to one broad at $\sim 457$ cm$^{-1}$ in the spectrum of pure TeO$_2$ glass. Below $400$ cm$^{-1}$, two broad bands can be resolved at $\sim 330$ and $\sim 120$ cm$^{-1}$ in the spectra of the glasses. The assignment of these spectral features will be followed in the next paragraphs.

For quantitative analysis the raw spectra have been subjected to the reduced representation according to equation:

$$I_{\text{red}}(\omega) = \frac{\omega [n(\omega, T) + 1] I_{\text{Exp}}(\omega)}{(\omega_L - \omega)^4}$$

$$n(\omega, T) = \left[ \exp \left( \frac{\hbar \omega}{k_B T} \right) - 1 \right]^{-1}$$

where the term in the fourth power is the usual correction for the wavelength dependence of the scattered intensity, $\omega$ is the Raman shift, and $\omega_L$ denotes the wave number of the incident radiation. The factor $n(\omega, T)$ describes the mean occupation number of a specific vibration at temperature $T$ in terms of the Bose-Einstein statistical description obeyed by phonons. $\hbar$ and $k_B$ are the Planck and Boltzmann constants, respectively. The use of the reduced representation is particularly important if the spectral changes brought about by either temperature or structural changes are to be disentangled. By applying Eq.(1), we get rid of the former and we are thus able to follow more accurately the latter.

Representative Stokes-side reduced spectra of $x\text{La}_2\text{O}_3-(1-x)\text{TeO}_2$ glasses are presented in a comparative way in Fig.3. The spectra have been normalized with respect to the $\sim 660$ cm$^{-1}$ peak intensity. It is seen that on going from $x=0$ to $x=0.25$ the intensity of the shoulder band at around $\sim 780$ cm$^{-1}$ is increased. In order to unravel the spectral features of the vibrational line...
profiles, the reduced spectra were fitted using Gaussian-distributions. The fitting was performed using the non-linear regression method based on the Levenberg-Marquardt algorithm. A representative example of the deconvolution procedure for pure TeO$_2$ glass is shown in Fig.3(b), where the complete fit of the pure TeO$_2$ spectrum is shown. Four Gaussian profiles are shown in the high-frequency spectral envelop (500–850 cm$^{-1}$) of TeO$_2$ glass. These bands are approximately located at 780, 730, 660, and 610 cm$^{-1}$. In the medium frequency range (400–500 cm$^{-1}$) one Gaussian profile, located at 457 cm$^{-1}$, can be resolved under the broad spectral envelop of the glass. Below 400 cm$^{-1}$, three broad bands can be resolved at $\sim$353, $\sim$294, and $\sim$162 cm$^{-1}$ in the spectrum of the glass.

The origin of the main bands appearing in the reduced Raman spectra of $x$La$_2$O$_3$-(1-$x$)TeO$_2$ glasses according to the deconvolution process (Fig.3(b)) can be assigned as follows. The bands at $\sim$780 and $\sim$720 cm$^{-1}$ have been assigned to stretching modes of TeO$_3$ tp units. The doublet at $\sim$670 and $\sim$620 cm$^{-1}$ has been assigned to the stretching modes of the TeO$_4$ tpb units. The two different peaks are presumably related to the two non-equivalent oxygen atoms (those at the equatorial plane and those out of the plane). Further, the two peaks at $\sim$500 and $\sim$450 cm$^{-1}$ are assigned to Te–O–Te and/or O–Te–O linkages [8, 19]. The existence of these bands indicates the presence of a continuous network consisting of vertex-sharing tellurium-oxygen polyhedra. The peaks observed at $\sim$330 and $\sim$120 cm$^{-1}$ in the low-frequency region are assigned to a bending vibration of TeO$_3$ tp having two or three non-bridging oxygen NBO atoms [8, 19].

Figure 4 shows the intensity ratio of the individual Gaussian profiles versus La$_2$O$_3$ content for the $x$La$_2$O$_3$-(1-$x$)TeO$_2$ glasses. There is a monotonic increase of the intensity ratio ($I_{780}^{+}+I_{730}^{+}$)/($I_{660}^{+}+I_{610}^{+}$) on the composition. The observed spectral changes with La$_2$O$_3$ composition imply that the population of the TeO$_4$ tpb units diminishes with increasing modifier content giving rise to an increased population of the TeO$_3$ tp units. The incorporation of higher modifier content in the glass structure creates larger free volume, which favors the transformation from TeO$_4$ tpb to TeO$_3$ tp.

The above proposed structural transformation is further supported by the composition dependence of the integrated intensities of the medium- and low-frequency Raman features presented in Fig.5. The integrated intensity of the 450 cm$^{-1}$ Raman band versus La$_2$O$_3$ composition shows a clear decrease, while the integrated intensities of the 330 and 120 cm$^{-1}$ bands exhibit the opposite trend. As reported previously, the Raman bands at $\sim$330 and $\sim$120 cm$^{-1}$ are assigned to TeO$_3$ tp having two or three NBO atoms, while the 450 cm$^{-1}$ band is attributed to Te–O–Te and/or O–Te–O linkages [8, 19]. The integrated intensity increase of the low-frequency bands reveals an increase of the TeO$_3$ tp population, while the intensity decrease of the medium-frequency band implies the gradual degradation of the tellurite network caused by modifier incorporation in the structure.

A model dealing with structural changes on the addition of network modifying oxides to TeO$_2$ glass has been proposed by Himei et al. [20]. In the context of this model, the transformation of TeO$_4$ tpb to TeO$_3$ tp...
is realized by means of the following equilibrium reactions:

\[ \text{TeO}_3/2 \leftrightarrow \text{TeO}_{2.5}/(=\text{O}) \]  

(3)

\[ \text{TeO}_3/2\text{O}^- \leftrightarrow \text{TeO}_{1.5}/(=\text{O}) \]  

(4)

here, we propose that the TeO$_3/2$O$^-$ (see both isomeric charged units in Fig.1 (b) and (c) and the TeO$_1/2$O$^-$(=O) units (see Fig.1(c)) are the basic coordination polyhedra, which are also present in tellurite crystals and both represented as 1/2[Te$_2$O$_3$]$^{2-}$ [20]. The meaning of the subscript in the TeO$_4/2$, TeO$_4/2$O$^-$, TeO$_3/2$(-O), and TeO$_1/2$O$^-$(=O) structural units is that four, three, two and one oxygen atoms respectively, are bridged with two other neighbouring atoms. Molecular orbital calculations on clusters modeling TeO$_2$ glass [21, 22], point out that for the TeO$_2/2$(-O) neutral unit (see Fig.1(d)), a band in the Raman spectrum around 900 cm$^{-1}$ should appear. However, such a feature is not observed in the Raman spectra of tellurite glasses.

The vitrification reaction can be described as:

\[ y\text{O}_{3/2}^2- + \text{TeO}_{4/2} \rightarrow a[\text{TeO}_{3/2}O^-] + b[\text{TeO}_{1/2}O^- (=\text{O})] + c[\text{TeO}_{2/2} (=\text{O})] + d[\text{TeO}_{4/2}] \]  

(5)

where $y=x/(1-x)$, $a$, $b$, $c$, and $d$ are parameters. If the TeO$_2/2$(-O) unit does not exist, then $c=0$. On the other hand, the ratio [TeO$_3$]/[TeO$_4$] is directly obtained from the Raman data. Since the glass composition $x$ is known, by applying the mass and charge balance, then the molar ratios of the structural units in tellurite based glasses can be determined. Thus, we are able from the modified vitrification reaction to calculate in lanthanum-tellurite glasses, the fractions of TeO$_4$ tbp with and without a non-bridging oxygen

(NBO), namely the TeO$_4/2$ and the TeO$_3/2$O$^-$ units and the fraction of TeO$_1/2$O$^-$(=O) tp unit with two NBO’s. The results are presented in Fig.6 for all compositions studied. Schematic representation of the structural mechanism is shown in Fig.1(f). The speciation plot of Fig.6 reveals that the population of TeO$_4/2$ decreases, while the TeO$_3/2$O$^-$ and TeO$_1/2$O$^-$(=O) units increase with increasing La$_2$O$_3$ content. Note that there is an hysteresis in the formation of TeO$_3/2$O$^-$ compared to TeO$_1/2$O$^-$(=O), which can be explained in the context of the resonance between the Te=O$^-$ and Te=O bonds. The TeO$_1/2$O$^-$(=O) unit (see Fig.1(e)) is more stable than the TeO$_3/2$O$^-$ unit (see Fig.1 (b) and (c)) and therefore is the main product at low La$_2$O$_3$ content.

In the context of this structural model the fraction of NBO’s to the total number of oxygen atoms can be calculated and the results are shown in Fig.7. These findings clearly reveal that lanthanum oxide modifier variation in the TeO$_2$ network leads to two type structural changes, namely the presence of three-coordinated Te atoms and the formation of NBOs.

The increase of the TeO$_1/2$O$^-$(=O) units with La$_2$O$_3$ variation causes a parallel increase of the repulsion between the lone pairs of electrons in the TeO$_1/2$O$^-$(=O) units, which further increases the relative stability of the TeO$_1/2$O$^-$(=O) units. Our findings are further supported by the work of Uchino et al. [21, 22], it was concluded that the TeO$_3/2$O$^-$ unit with one NBO was present most probably as the TeO$_3/2$O$_{ax}$- unit with the terminal oxygen atom in the equatorial site and the TeO$_3/2$O$_{a}$- units with the terminal oxygen atom in the axial site were easily transformed into the TeO$_1/2$O$^-$(=O) trigonal pyramid units. We propose that the addition of a modifying oxide into the tellurite network causes a breaking of the Te$_{ax}$-O$_{ax}$-Te linkages, thereby reducing the constrains of the network. Therefore, tellurite glasses are easily vitrified by the addition of a network modifying oxide. However, the excessive
addition of a network modifier reverses the process and makes vitrification at a high La$_2$O$_3$ composition difficult.

From the distribution of the basic structural units of the tellurite network, we are able to calculate the composition dependence of density by employing a model proposed by Feller and co-workers [23]:

$$d(x) = \frac{\sum M_i X_i(x)}{\sum V_i X_i(x)}$$  \hspace{1cm} (6)

where $M_i$, $X_i$, and $V_i$ are the molar mass, mole fraction and effective molar volume of the $i$th local structural unit. The mole fractions of the various short-range order units are reported in Fig.6, while molar volumes have been derived from the best fitting to the experimental density data. The results of the non-linear least square fit of Eq.(6) to the experimental density data, assuming that the volumes $V_i$ are composition independent, are shown in Fig.8. It is clear that $x<0.20$ the simulated results agree quite well with the experimental data, whereas above this composition the agreement is not so good. This finding indicates that the knowledge of the short-range order structure, as expressed by the $X_i$ fraction of the local tellurite polyhedra, is not sufficient to simulate the monotonic, almost linear, density profile in terms of the present model. The above calculation is independent of any assumption made in the context of the tellurite network model and appears to be more reliable. The fairly good agreement between the experimental density and the calculated values estimated directly from Raman spectroscopic measurements using Eq.(6) indicates that the structural mechanism proposed in this work concerning the tellurite polymorphs is valid.

**IV. CONCLUSION**

A detailed Raman spectroscopic study of lanthanum tellurite glasses in the entire glass-forming range has been conducted. The modifier-induced structural modifications have been unveiled by estimating the population of the basic structural polymorphs present in these glasses in a quantitative manner for the first time.

The analysis of the reduced polarized Raman spectra allows us to quantitatively follow the well-established transformation of the TeO$_4$ trigonal bipyramids into TeO$_3$ trigonal pyramids with lanthanum oxide variation. It is proposed that the presence of neutral trigonal pyramid TeO$_{2/2}$($=O$) units in these tellurite-based glasses is questionably based on the lack of any spectroscopic evidence. The distribution of tellurite polymorphs revealed that the estimated fraction of TeO$_4$ tp with all oxygen atoms bridged decreases, while the fractions of TeO$_4$ tp and TeO$_3$ tp with one and two non-bridging oxygen atoms, respectively, display a parallel increase with increasing La$_2$O$_3$ content. The competition between TeO$_{3/2}$O$^-$ and TeO$_{1/2}$O$^-$($=O$) units with increasing modifier content can be explained considering the repulsion between the lone pairs of electrons of excessive TeO$_{1/2}$O$^-$($=O$) trigonal pyramid groups. The addition of lanthanum modifier to the tellurite glass matrix leads to a gradual transformation of TeO$_{4/2}$ to TeO$_{3/2}$O$^-$ initially, and then to TeO$_{1/2}$O$^-$($=O$) trigonal pyramid depending on the modifier content. The spectroscopic data are adequate for calculating the fraction of the terminal oxygen atoms based on the proposed structural mechanism. The relative amounts of the species involved in the structural changes with composition have been used in the context of an existing density model to sufficiently simulate the experimental density of these lanthanum tellurite glasses.

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