

Manifestation of thermodynamic glass transition by structure and picosecond dynamics in alkali tellurite glasses

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ARTICLE INFO

Article history:

Received 16 May 2012

Received in revised form 6 July 2012

Available online 26 July 2012

Keywords:

Tellurite glasses;
Glass-transition;
Raman spectroscopy;
Dimensionality;
Boson peak

ABSTRACT

The Raman spectra of the $0.1\text{Cs}_2\text{O}-0.9\text{TeO}_2$ melt were measured and analyzed over a broad temperature range including the glassy, supercooled and molten state in an effort to follow the varying structural and dynamical aspects caused by temperature and alkali modifier. The network structure of the glass/melt is formed by mixing TeO_4 trigonal bipyramid and TeO_3 trigonal pyramid units. Changing alkali content and/or temperature results to conversion of the TeO_4 units to TeO_3 units with a varying number of non-bridging oxygen atoms. The low-frequency Raman spectra reveal a well-resolved Boson peak whose frequency also depends on temperature. The variation of the maximum of the Boson peak has been determined and discussed in the framework of current phenomenological models. The short-time dynamics of the system experiences drastic changes when approaching the glass-to-liquid transition. The temperature dependent plot of the correlation times extrapolates to a crossover value, which we assign as spectral evidence of the system's known thermodynamic glass transition temperature. Similar behavior exhibit several spectral features, such as the maximum of the Boson peak, the exponent of the susceptibility and the intensity ratio related to the structural transformation from TeO_4 tbp to TeO_3 tp species occurring in the medium range order structure.

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1. Introduction

Tellurite based glasses belong to a class of materials that have been arousing a great deal of 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]. Much work has been done concerning their special applications as non-linear optical materials [4]. The spatial, dynamical properties and the understanding of nature of quantized excitations in fractal networks, such as the tellurite network, have been proved a very fertile field of research over the past decades [5]. The dynamics of fractal networks has been used as a model to aid the understanding of thermodynamic properties of several systems [5]. It is widely accepted that the glass structure has a certain dimension, although the quantitative estimation of structural dimensionality has not been made yet.

The structure of pure TeO_2 and tellurium oxide based glasses has been studied with a variety of spectroscopic and diffraction techniques (see e.g. Refs. [6–14]). The outcome of these studies pertains to two basic findings: first, the pure TeO_2 consists of TeO_4 trigonal bipyramids (tbp's), 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. Second, the addition of alkali and/

or alkaline earth modifiers to pure TeO_2 network causes a change in the Te coordination polyhedron from TeO_4 tbp to TeO_3 trigonal pyramid (tp) in which one of the Te sp^3 hybrid orbitals is occupied by a lone pair of electrons [6–14]. Recently, the intramolecular and intermolecular dynamics have been studied in tellurite based glass-forming system [15]. However, a limited number of papers have been focused on the concept that the vibrational energy levels and therefore vibrational frequencies experience the influence of their immediate environment when going from isolated to a more condensed phase and the energy flow mechanisms into and out of a molecule.

In the present paper, we will address the issue of the applicability of the microscopic dynamics emerging from vibrational dephasing studies as a sensitive indicator of the thermodynamic glass transition in alkali tellurite glasses. To accomplish our task, we have employed a temperature dependent Raman spectroscopic study for the $0.1\text{Cs}_2\text{O}-0.9\text{TeO}_2$ binary glass-forming system in glassy, supercooled and molten states. Intramolecular vibrational modes have been analyzed using a specific methodology in order to extract time-correlation functions without the use of Fourier transform. This approach allowed us to avoid all the inaccuracies that Fourier transform techniques convey when performed in noisy and overlapping vibrational bands.

2. Experimental details

The reagent grade chemicals tellurium (IV) oxide (99.99% purity) and cesium carbonate (99.95% purity) were purchased from Alfa

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Aesar. The appropriate amounts of polycrystalline TeO_2 and Cs_2CO_3 were mixed and melted in platinum crucibles at 700–800 °C for 15–30 min. Short time is crucial to avoid changes of the melt composition. The homogenized bubble-free liquids were quenched using the conventional method by dipping the crucible into cold water.

Raman spectra were recorded using the 514.5 nm line of an Ar^+ laser as excitation source in a backscattering geometry using a microscope objective (50×/0.55). The specimen was placed in a hot stage (Linkam THMS600) with controllable temperature, appropriate for use under microscope. The scattered light was resolved by a triple monochromator Jobin Yvon T64000 set at the double subtractive mode configuration for better stray light rejection and for sharp cut-off of the exciting laser line at low frequencies. The three holographic gratings installed were of 1800 grooves/mm and their diffraction efficiency was optimized at 2 cm^{-1} to increase signal quality. The analyzed light was detected by a two-dimensional charge-coupled device (CCD) detector with 1024×256 pixels and cooled at 140 K for thermal noise reduction. Both polarized (VV : vertical polarization of incident laser–vertical analysis of scattered light) and depolarized (VH : vertical polarization of incident laser–horizontal analysis of scattered light) scattering geometries were employed for glasses. This was achieved with the aid of a set of Glan and Glan-Thompson polarizers (Hale) with extinction coefficients better than 10^{-6} and 10^{-7} , respectively. Stokes-side Raman spectra were recorded from room temperature up to 600 °C. The temperature controller of the THMS600 hot stage was able to maintain the temperature during each measurement fixed, with stability better than 0.1 °C. A calibration procedure with the aid of a CCl_4 sample was often taking place in order to check the polarization and correct for possible drifts of the monochromator's gratings. Accumulation times were adjusted to result in a very high signal-to-noise ratio; few minutes depending on the sample temperature were sufficient for this.

3. Results and discussion

3.1. Effect of the alkali metal modifier and temperature on the glass structure

In order to quantitatively follow the observed temperature induced spectral changes, the reduced representation of the raw data has to be taken into account according to equation:

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

where the term in the fourth power is the usual correction for the wavelength dependence of the scattered intensity; ω is the Raman shift in cm^{-1} , and ω_L denotes the wave number of the incident radiation. The factor $n(\omega, T) = [\exp(\hbar\omega/k_B T) - 1]^{-1}$ 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 either by 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. Details concerning the use of the reduced representation in heat-induced structural changes can be found elsewhere [16,17].

To avoid any further implications of possible different degrees in the symmetry of the vibrational modes we further proceed to the comparison of the isotropic Raman intensity, defined as:

$$I_{\text{ISO}}(\omega) = I_{\text{VV}}(\omega) - (4/3)I_{\text{VH}}(\omega). \quad (2)$$

The isotropic intensity separates the scattered intensity caused by the diagonal elements of the Raman scattering tensor from the

corresponding intensity caused by the off-diagonal elements [anisotropic spectrum, $I_{\text{ANISO}}(\omega) = I_{\text{VH}}(\omega)$].

Representative Stokes-side reduced, isotropic spectra of 0.1 Cs_2O –0.9 TeO_2 glassy, supercooled and molten states in Fig. 1. In order to unravel the spectral features of the vibrational line profiles, the reduced isotropic spectra were deconvoluted using Gaussian-type distributions. Four Gaussian profiles are shown in the high-frequency spectral envelop (500–850 cm^{-1}) of the room temperature glass. These bands are approximately located at 780, 720, 670 and 620 cm^{-1} . These bands are illustrated in Fig. 1 as D, C, B and A, respectively. In the medium frequency range [400–500 cm^{-1}] two Gaussian profiles, located at 500 and 470 cm^{-1} , can be resolved under the broad spectral envelop of the glass, while above melting point one at ~ 472 cm^{-1} broad peak dominates this frequency range. Below 400 cm^{-1} , two other broad bands can be resolved at ~ 300 and ~ 170 cm^{-1} in the isotropic spectra of the glass and melt.

In brief, the TeO_2 glass is composed of TeO_4 trigonal bipyramid units (tbp), where one of the equatorial sites is occupied by a lone pair of electrons, and most of the tellurium atoms are connected at vertices by $\text{Te}_{\text{equatorial}}\text{O}_{\text{axial}}\text{Te}$ linkage [18]. This linkage connects two distinct tbp units, where the oxygen atom is in equatorial (short bond distance) for the first and in axial site (long bond distance) for the second tbp unit, respectively. Thus, TeO_2 glass has a unique structure owing to these units and its connecting style considerably differs from the conventional glass formers, such as B_2O_3 , SiO_2 , GeO_2 and P_2O_5 . TeO_2 may have a structural role differing than that of other conventional oxides in binary glasses which contain network modifiers. Many authors have proposed, based on Raman spectroscopic results, that the primary structural unit of tellurite glasses having high TeO_2 content is a distorted TeO_4 tbp and that the fraction of TeO_3 trigonal pyramids (tp) increases with increasing the content of mono- or di-valent cation oxides, which act as network modifiers [8,19–22].

The origin of the main bands appearing in the reduced isotropic Raman spectrum of 0.1 M_2O –0.9 TeO_2 glasses according to the

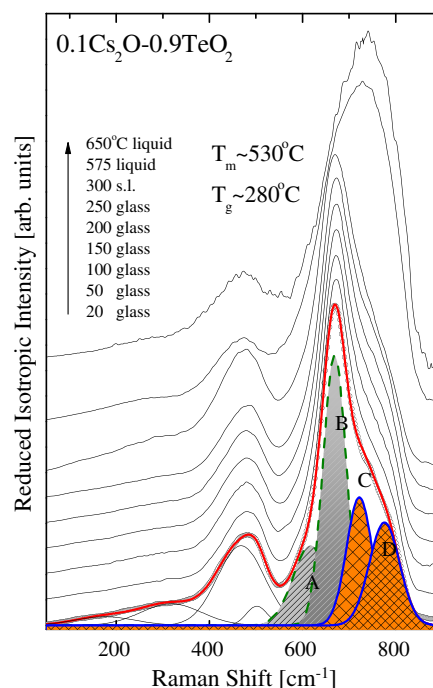


Fig. 1. Temperature dependence of the reduced isotropic Raman spectra for the 0.1 Cs_2O –0.9 TeO_2 glass in a wide range covering the glassy, supercooled and liquid state. Deconvoluted individual vibrational lines are shown for the room temperature spectrum. Open circles: experimental data (only 33% of the experimental points are shown for clarity). Thick solid lines: total fit curve. Gaussian lines: individual vibrational peaks. Spectral conditions: excitation line: 514.5 nm, laser power: 400 mW, resolution: 2 cm^{-1} , and CCD detector (s.l. = supercooled liquid).

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