Analysis of Physical and Structural Properties of Alkali Oxide–Modified Tellurite Glasses

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Abstract. Glasses in the system $x \, M_2O \cdot (1-x) \, TeO_2$ ($0 \le x \le 0.25$), where M = Li, Na, K, Rb, Cs, were made by melting in platinum crucibles. Various quenching methods were used to make each glass because some glasses require extremely rapid cooling. Physical properties such as the glass transition onset temperature (T_g) and density (ρ) were measured. In order to explore the short-range structure in these glasses, Raman spectroscopy, infrared spectroscopy, and high-energy x-ray diffraction were used. These experiments on tellurite glasses were performed to find correlations between the physical and structural properties.

INTRODUCTION

Pure tellurium dioxide glass was once perceived as impossible to make in bulk quantities. The only methods of forming this glass were by roller quenching or aero-levitation, making only hundredths of a gram of sample at a time.[1] However, Tagiara et al. developed the new intermittent quenching technique (IQ technique), which can produce pure amorphous TeO_2 in gram quantities.[2] The IQ technique involves dipping the bottom of the crucible in and out of water rapidly in a controlled manner. This hard-to-make glass has shown unusual physical and chemical properties in comparison to other oxide glasses, which makes this a very sought-after material for research. These characteristics include a high refractive index and dielectric constant, low phonon energy and melting temperature, excellent third-order nonlinear optical properties, and a large thermo-optic coefficient.[3–8] Based on these data, tellurium dioxide glasses are favorable materials for numerous optical devices, such as erasable optical recording media,[9] optical switching devices,[10] or lenses and fibers for near-infrared applications. However, since there still exists disagreeing results of the coordination number of tellurium, n_{TeO}, there is still much to test to find an agreement on what the data are conveying. The coordination number of Te and its number of bridging oxygens is denoted as Q_m^n, where the index n gives the number of bridging oxygens bonded to the central atom and m gives the coordination number.[11] The resulting Q_m^n for each tellurite polyhedron can be found in Fig. 1.

Studies from various techniques such as neutron diffraction[1] (ND) and Raman spectroscopy[12] show that pure amorphous TeO_2 has a mixture of approximately two-thirds TeO_4 units and one-third TeO_3 trigonal pyramids, but this answer still remains uncertain. One nuclear magnetic resonance (NMR) study[13] has not found any evidence of TeO_3 units, which differs from another NMR result[14] where TeO_3 or TeO_{3+1} units were recorded (where TeO_{3+1} refers to 4 coordination with one longer bond). In addition, a recent high-energy x-ray diffraction study of TeO_2 glass has shown the presence of Q_4^4 units.[15] TeO_3 units may show the existence of terminal oxygens in the glass structure and cause a decrease in coordination number. A 2000 study from McLaughlin et al. suggests that only Q_4^4 and Q_4^3 exist of the possible 4-

coordinated tellurium, because species like Q_4^2 would require a change in the oxidation state of tellurium, which was not observed.[11] This is mostly consistent with the NMR study by Marple et al., which found the coordination number to be 3.89.[14] Although it is often assumed that Te in pure a-TeO$_2$ is 4 coordinated, analogous to crystalline polymorphs of TeO$_2$, the average n_{TeO} decreases as the amount of modifier is added through the intermediate formation of TeO$_{3+1}$ until the tellurium is entirely 3 coordinated.[1] The lowering of the coordination number can be seen as less than 4 for glasses with as little as 1 mol % modifier alkali oxide. The active lone pair of electrons on the tellurium atoms induces a pseudo-trigonal bipyramid structure in α-TeO$_2$. This can suggest that a-TeO$_2$ is composed of asymmetric [TeO$_4$] units with two short (1.882 Å) equatorial and two long (2.177 Å) axial Te-O bonds.

EXPERIMENTAL PROCEDURES

FIG. 1. Left: Q_m^n, where m = 3,4 identifies the total number of oxygen bonded to the tellurium atom and n = 0–4 is the number of bridging oxygen bonded to the tellurium atom.[11] Right: Tellurium dioxide crystal (left). Pure tellurium dioxide glass made with IQ technique (right).

All glasses for x-ray studies at the Advanced Photon Source (APS) at Argonne National Lab were made using Sigma Aldrich chemicals of ≥99% purity (see Fig. 1 for TeO$_2$). Lithium, sodium, and potassium tellurite glasses were formed up to 25 mol % modifier by heating the alkali carbonate and tellurium dioxide mixture in a platinum crucible for 10 min at 800ºC twice. After the first melt, the contents were cooled outside of the furnace. Once cooled the weight loss was recorded, subtracting off the crucible weight. The roller-quenched glasses were ideal for loading into the capillaries for x-ray diffraction. Once the second melt had finished, it was immediately poured into a stainless-steel roller quencher, which yielded mostly glass. This resulted in thin transparent yellow pieces of glass. Half of the glass made was stored in a nitrogen-sealed glove box and the other half was directly taken to measure T_g. The glasses stored in the glove box were eventually taken to the APS for high-energy x-ray diffraction measurements.

Glasses for infrared and Raman spectroscopy at the National Hellenic Research Foundation were made using Sigma Aldrich chemical of ≥99% purity. Glasses modified with M$_2$O (M=Li, Na, K, Rb, Cs) were made from 5–25
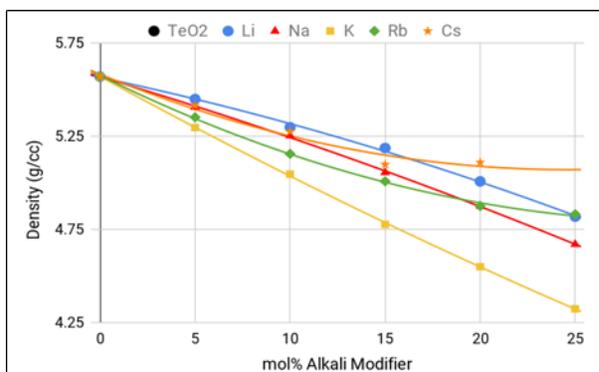

FIGURE 2. Densities of alkali tellurite glasses vs. mol % of alkali oxide.

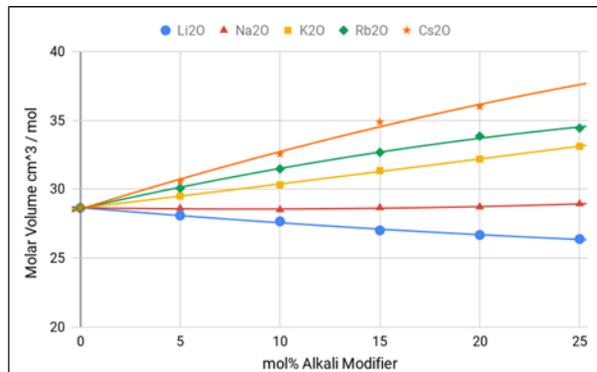**FIGURE 3.** Molar volume of alkali tellurite glasses vs. mol % of alkali oxide.

mol % of modifier oxide. However, Cs_2O-TeO_2 could not be made at 25 mol % modifier. These glasses were melted in a platinum crucible for 15 min at 1000°C for M=Li, Na, Rb, Cs and 15 min at 800°C for M = K. Then the contents cooled in the crucible without any sort of quenching aid. Glasses were easily formed and came out of the crucible in a coinlike shape, which was most suitable for infrared and Raman polishing and signal gathering.

Differential scanning calorimetry (DSC) was used to find the glass transition onset temperature. Samples were ground into a powder and crimped tightly into an aluminum pan while in a nitrogen glove box. DSC was then performed at 40°C/min in air on all samples immediately after formation to avoid water absorption. Glass onset temperature (T_g) and crystallization temperature (T_x) were measured on a Perkin Elmer DSC 7. DSC results were reported at the 2019 International Congress on Glass.
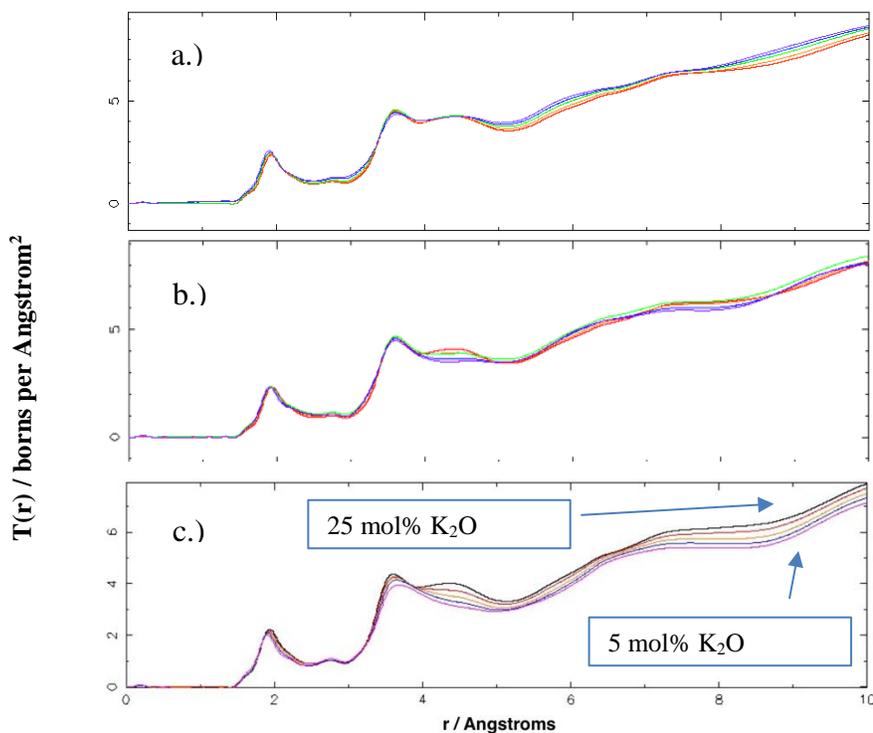

FIGURE 4. Total correlation functions from x-ray diffraction analysis: (a) Li_2O-TeO_2, (b) Na_2O-TeO_2, and (c) K_2O-TeO_2. The following was observed: Short Te−O bonds (1.85−1.88 Å) and a longer Te−O bond and O-O bond at (2.5−2.9 Å). The different colored lines represent the various mol % of alkali oxide in the glass. The alkali content increases such that 5 mol % of alkali oxides is the bottom line and 25 mol % is the top line, as shown in Fig. 4c.

Density was found using a Quantachrome Ultrapyc 2000e automatic helium pycnometer. Pellets of aluminum were loaded into a calibrated sample chamber of known volume. Helium was introduced and the pycnometer measured the volume of the sample 15 times. Then the last five measurements were averaged together to find the average volume of the sample. Since the density of aluminum is known, 2.698 g/cm^3,[16] we used this as our reference of 15 runs of aluminum, 15 runs of our glass sample, and another 15 runs of aluminum. Our average densities can be found in Fig. 2, while molar volumes are shown in Fig. 3.

High-energy x-ray diffraction measurements were made at beamline 6-ID-D of the Advanced Photon Source at Argonne National Lab. Roller-quenched samples of M_2O-TeO_2 (M=Li, Na, K) glasses were powdered with a mortar and pestle and loaded into thin walled borosilicate glass capillaries of 1.5 mm internal diameter. The diffraction pattern was recorded using an incident beam energy of 100.36 keV and a flat-panel Varex 4343CT detector (2880 × 2880 pixels of 150 × 150 μm) for a total of 15 min. The capillary was also measured for the background subtraction. The sample-to-detector distance of 346.9 mm was calibrated by measurement of a sample of NIST standard CeO_2. Each sample was tested for a total of 135 min. The powder patterns from the x-ray diffraction were obtained using the Fit2D program. All tests for each sample were averaged together and the powder pattern was then read. Once the powder patterns were made, the files were converted to an .XYE file and uploaded to GudrunX[17] to make further corrections

to the x-ray data, for example, absorption, background, fluorescence, density, abundance, and calibration factors. X-ray structure factors obtained using GudrunX were then Fourier transformed to obtain the total correlation functions using software provided by Dr. Alex Hannon. The total correlation function was then found to measure the bond lengths between tellurium to oxygen, tellurium to tellurium, and oxygen to oxygen in every M_2O (M=Li, Na, K) modified tellurite glass, see Fig. 4.
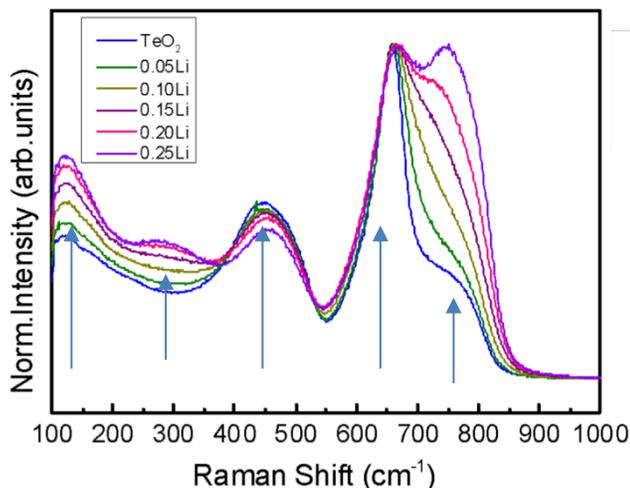
RESULTS AND DISCUSSION

FIGURE 5. Raman spectra for Li-TeO$_2$ glasses.

Molar volume is shown in Fig. 4. This graph makes sense, because as the modifier cation gets larger, the molar volume increases. The total correlation functions are consistent with a distribution of Te-O bond lengths over a very wide range. The coordination of tellurium is consistent with 4. Since there is a wide distribution, this can be thought of as 3+1.

Raman spectra for a representative glass system (Li) are shown in Fig. 5. The first peak at around 120 cm^{-1} is known as a notch filter artifact. The second set of peaks at around 295 cm^{-1} is probably related to Li+ motion. Also, network deformations are expected around this frequency range. The peak at around 450 cm^{-1} is the symmetric stretching/bending vibrations of Te-O-Te bridges. At 660 cm^{-1} the stretching of TeO$_4$ units is observed. Scattering above 700 cm^{-1} is due to the asymmetric stretching of the Te-O-Te bridges connecting tellurite units. The stretching of the TeO$_3$ units formed by adding the modifier oxide, Li$_2$O, to TeO$_2$ content was seen.
Infrared spectra are not shown here due to space limitations and will be reported at a future Glass and Optical Material Division meeting of the American Ceramic Society.

CONCLUSIONS

Alkali tellurite glasses were studied by XRD, Raman spectroscopy, infrared spectroscopy, and molar volume determination. The results form a structural picture in which tellurium was found to be 4 coordinated in a form likely of three short Te-O bonds and one longer Te-O bond. As alkali oxide modifies the glass, nonbridging oxygens are created at the expense of bridging oxygens. The present XRD results confirm previous NMR and high-energy x-ray diffraction studies where the coordination of tellurium was found to be near 4 in TeO$_2$ glass.[13,14] As the glass is modified, the tellurium changes its coordination number from 4 to 3.

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