

Properties and Structure of Glassy TeO₂ and Binary Potassium and Boron Tellurites

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Abstract. Tellurite glasses show potential for use in mid-infrared optical applications¹, but their structure has not been intensively studied. While they do not conduct light better than chalcogenides, which are currently the best glasses for infrared optics, they are much easier to produce. Potassium and boron tellurite glasses, including single component, rapidly cooled TeO₂, are reported and studied here. The results include the Glass Transition Temperature (T_g) measurements and Raman spectra. Proposed structural models are also discussed.

Keywords: Glass Structure, Glass Transition Temperature, Raman Spectroscopy, Tellurites

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INTRODUCTION

Tellurium dioxide (TeO₂) is a conditional glass former and the application of rapid cooling through the twin roller technique has enabled glass formation to a limited extent. Modification of tellurium by boron oxide and potassium oxide results in much easier glass formation with slower cooling rates, and consequently, produces higher glass yield.

In this paper we report on physical properties and structure of these tellurite glasses, including measurements on single phase TeO₂ glass. The physical properties measured were the glass transition temperature (T_g) and the crystallization temperature (T_x). Raman spectroscopy was used to infer structural information.

Most glass forming oxides have a coordination number that is a whole number and a glassy structure that is similar to the corresponding crystalline structure. Originally, it was assumed that tellurium dioxide also followed this trend, but according to neutron scattering and Raman spectroscopy, that does not seem to be the case.¹ Instead of the pure glass consisting of only four coordinated units (where the tellurium is bonded to four oxygen atoms), it also includes three coordinated units (where the tellurium is bonded to three oxygen), as shown in Figure 1. Most likely, the pure TeO₂ glass forms in about two-thirds four coordinated units and one-third three coordinated units with a double bonded oxygen, due to a broad distribution of Te-O bond lengths and asymmetrical bonds.¹

EXPERIMENTAL PROCEDURE

Glass Preparation

The glasses were made from reagent grade or better tellurium dioxide, boric acid, and potassium carbonate. The boron tellurites, potassium tellurites, and pure TeO₂ glasses were made in 4 to 10 gram well-mixed batches. The batches were heated at 800 °C for 10 minutes, after which a weight loss was determined, and the glass was heated at the same temperature for another 10 minutes, at which point the samples were quenched into glasses as described below.

All samples were made and heated in platinum crucibles. Glasses were roller quenched², which produced clear yellow or orange tinted glasses, likely due to small amounts of platinum contamination in the ppm range.³ The cooling rate was about 500,000 ± 100,000 °C/s.

Thermal Measurements

Thermal measurements using differential scanning calorimetry (DSC) were performed by heating from room temperature at 40 °C/min to 400 °C using a TA model Q200 Differential Scanning Calorimeter. The onset method was used to determine the T_g. A baseline was run before every measurement and the instrument was calibrated frequently. The error in the reported T_g is approximately ± 3 °C.

Raman Measurements

Raman spectroscopy was run using a JASCO NRS-3100 Laser Raman Spectrophotometer with a 785 nm laser, employing a silicon crystal reference for calibration at 520.52 cm^{-1} . The sample was focused using a 5x, 20x, and 50x lens successively and the intensity of the laser was optimized to minimize noise. Two 30 second runs were averaged to eliminate cosmic ray events.

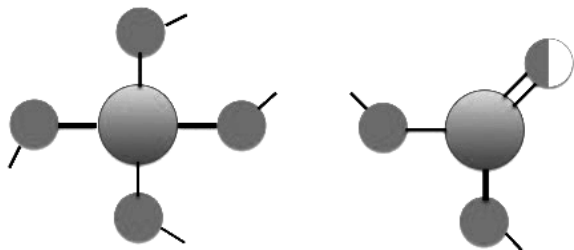


FIGURE 1. A four-coordinated unit shown on the left and a three-coordinated unit on the right. The larger circles are the tellurium atoms while the smaller circles are the oxygen.

RESULTS

Table 1 lists all T_g and T_x results obtained from DSC measurements. T_g results from pure amorphous TeO_2 were prepared using roller quenching. In Figure 2, the T_g was shown to be $305 \pm 3\text{ }^\circ\text{C}$, consistent with trends/extrapolations from other families of doped tellurium glasses that have been studied and with a recent report from the Kamitsos group by Tagiara et al.⁴

Raman spectroscopic results from pure TeO_2 and boron tellurites were obtained to verify glassiness and to determine structure. This was done for 3, 2, 1, 0.5, and 0.25-mol % B_2O_3 . To see whether the amount of modifier changed the structure of the glass, Raman spectra were compared for the doped samples and the pure TeO_2 sample. Spectra from the pure TeO_2 glass were compared to that of 0.25-mol % B_2O_3 as well. No discernable difference was noticed between them; all were glassy and similar to Figure 3, which shows pure TeO_2 glass and the alpha phase TeO_2 crystal. The peaks in the spectrum from the crystal are sharp and narrow, which we would expect, and the peaks from the glass are broader due to the disordered nature of the amorphous sample.

TABLE 1. Glass transition and crystallization temperature results from tellurites studied in this paper. All results were obtained from DSC measurements.

| Sample | $T_g \pm 3\text{ }^\circ\text{C}$ | $T_x \pm 3\text{ }^\circ\text{C}$ |
|---|-----------------------------------|-----------------------------------|
| Pure TeO_2 (yellow) | 305 | 348 |
| | 307 | 348 |
| Pure TeO_2 (orange) | 310 | 327 |
| $0.03\text{K}_2\text{O}-0.97\text{TeO}_2$ | 302 | x |
| | 302 | 335 |
| | 302 | 346 |
| $0.02\text{K}_2\text{O}-0.98\text{TeO}_2$ | 302 | 339 |
| | 302 | 339 |
| | 303 | 333 |
| $0.01\text{K}_2\text{O}-0.99\text{TeO}_2$ | 304 | 323 |
| | 304 | 323 |
| | 304 | 332 |
| $0.03\text{B}_2\text{O}_3-0.97\text{TeO}_2$ | 315 | 358 |
| | 312 | 354 |
| | 313 | 361 |
| | 314 | 351 |
| $0.02\text{B}_2\text{O}_3-0.98\text{TeO}_2$ | 311 | 360 |
| | 311 | 359 |
| $0.01\text{B}_2\text{O}_3-0.99\text{TeO}_2$ | 308 | 342 |
| | 309 | 346 |
| $0.005\text{B}_2\text{O}_3-0.995\text{TeO}_2$ | 307 | 343 |
| | 307 | 337 |

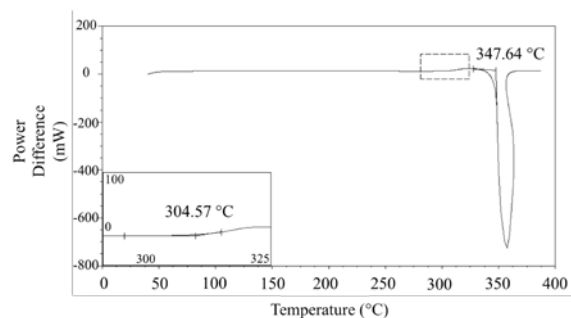


FIGURE 2. DSC curve from a sample of pure TeO_2 . The T_g is shown to be $305\text{ }^\circ\text{C}$ (see insert) and the T_x is $348\text{ }^\circ\text{C}$.

Figure 4 shows the T_g s and T_x s of boron tellurites with 3, 2, 1, 0.5, and 0 -mol % B_2O_3 . By applying a linear fit to the extrapolated data, the T_g and T_x of pure amorphous TeO_2 were estimated to be around $306\text{ }^\circ\text{C}$ and $340\text{ }^\circ\text{C}$, respectively. The T_g extrapolated was within error of the measured TeO_2 T_g of $305 \pm 3\text{ }^\circ\text{C}$, while the T_x was a little farther away from $348 \pm 3\text{ }^\circ\text{C}$, as seen in Figure 2. The T_g and T_x are fairly close, meaning that very high cooling rates need to be reached for glass formation.

CONCLUSIONS

While it is possible to produce small amounts of pure TeO_2 glass via the roller quencher, it is not a feasible method for large-scale fabrication. Instead, a

water quenching technique has been used to create 0.6 to up to 3 gram samples.^{4,6} This larger sample size will allow for a greater variety of structural tests to be run.

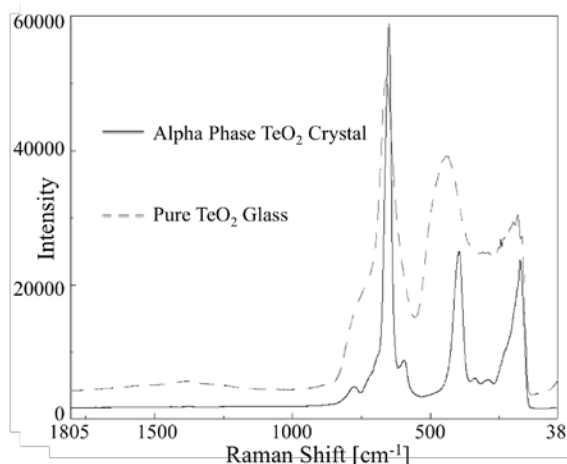


FIGURE 3. Overlaid Raman spectra from pure TeO₂ glass and the alpha phase TeO₂ crystal. The glass spectrum has broad peaks, which are indicative of a disordered structure, compared to the sharp peaks of the crystal.

DSC results for pure TeO₂ place the T_g at approximately 305 °C, which is consistent with the extrapolation of trends from the families of borate, potassium, and barium tellurites and other literature values. In addition to thermal measurements, coordination numbers of TeO₂ for the barium and strontium tellurite systems were calculated using Raman data (not included in this paper). The barium tellurites show a decreasing trend in Te coordination as the modifier is added, which is believed to occur because the increase in barium content adds non-bridging oxygens in the tellurite system. The strontium tellurite system shows a similar behavior. The most interesting result to notice, however, is that most of the trends of both families point to the coordination number of pure TeO₂ being approximately 3.7, which is consistent from values found in the literature.^{1,5} Looking at the coordination number of pure SiO₂ glass, which is 4, this could explain why pure tellurium glass is so difficult to produce. Instead of having an even number of similarly sized bonds, as in SiO₂, TeO₂ most likely has bonds that are asymmetrical in length, thus making a cohesive short-range order harder to achieve.

One possible route to better study the amorphous TeO₂ structure is to use the gamma phase crystal, as preliminary work suggests it matches the structure of the glass better than the alpha phase crystal.⁷ For further study of this, gamma phase crystal must be produced by heat-treating small samples of pure

TeO₂ glass, as those are the conditions where this crystal has been formed.^{1,7} There are also more glasses in the alkaline earth tellurite families that may be studied by roller quenching, specifically the calcium and magnesium systems.

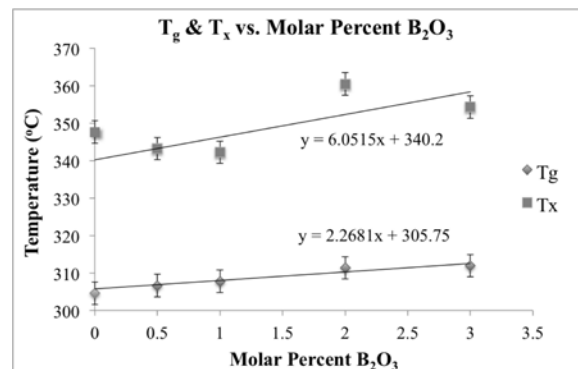


FIGURE 4. T_gs and T_xs of doped B₂O₃ tellurite glasses. The trend extrapolated from this data was used to predict the T_g of pure amorphous TeO₂. The measured T_g and T_x of pure TeO₂ have since been added.

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