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# Properties and Structure of Glassy TeO<sub>2</sub> and Binary Potassium and Boron Tellurites

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**Abstract.** Tellurite glasses show potential for use in mid-infrared optical applications<sup>1</sup>, 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 TeO<sub>2</sub>, are reported and studied here. The results include the Glass Transition Temperature (T<sub>g</sub>) measurements and Raman spectra. Proposed structural models are also discussed.

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

**PACS:** 81.05.Kf, 81.70.Pg, 42.55.Ye

## INTRODUCTION

Tellurium dioxide (TeO<sub>2</sub>) 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 TeO<sub>2</sub> glass. The physical properties measured were the glass transition temperature (T<sub>g</sub>) and the crystallization temperature (T<sub>x</sub>). 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.<sup>1</sup> 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 TeO<sub>2</sub> 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.<sup>1</sup>

## 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 TeO<sub>2</sub> 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.

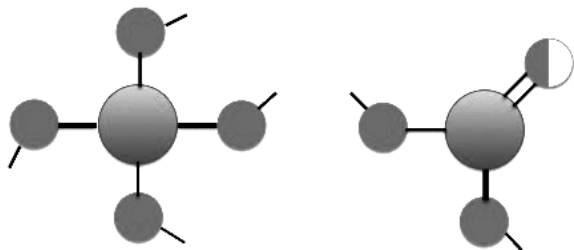
All samples were made and heated in platinum crucibles. Glasses were roller quenched<sup>2</sup>, which produced clear yellow or orange tinted glasses, likely due to small amounts of platinum contamination in the ppm range.<sup>3</sup> The cooling rate was about 500,000 ± 100,000 °C/s.

### 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<sub>g</sub>. A baseline was run before every measurement and the instrument was calibrated frequently. The error in the reported T<sub>g</sub> 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  $520.52\text{ cm}^{-1}$ . 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.

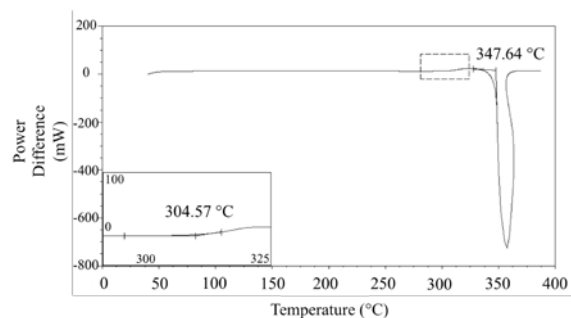
## RESULTS

Table 1 lists all  $T_g$  and  $T_x$  results obtained from DSC measurements.  $T_g$  results from pure amorphous  $\text{TeO}_2$  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.<sup>4</sup>

Raman spectroscopic results from pure  $\text{TeO}_2$  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 %  $\text{B}_2\text{O}_3$ . To see whether the amount of modifier changed the structure of the glass, Raman spectra were compared for the doped samples and the pure  $\text{TeO}_2$  sample. Spectra from the pure  $\text{TeO}_2$  glass were compared to that of 0.25-mol %  $\text{B}_2\text{O}_3$  as well. No discernable difference was noticed between them; all were glassy and similar to Figure 3, which shows pure  $\text{TeO}_2$  glass and the alpha phase  $\text{TeO}_2$  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 $\text{TeO}_2$ (yellow)	305	348
	307	348
Pure $\text{TeO}_2$ (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



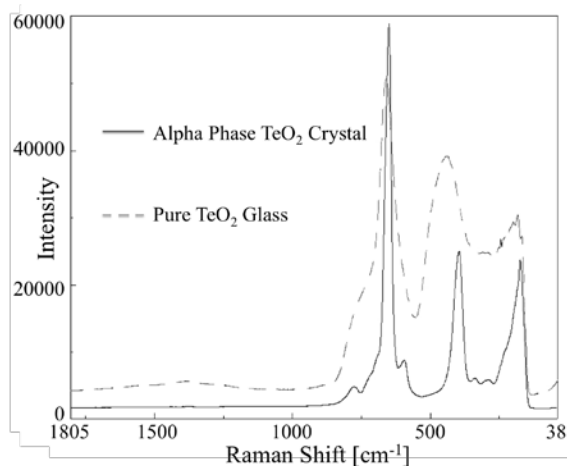
**FIGURE 2.** DSC curve from a sample of pure  $\text{TeO}_2$ . The  $T_g$  is shown to be  $305\text{ }^\circ\text{C}$  (see insert) and the  $T_x$  is  $348\text{ }^\circ\text{C}$ .

Figure 4 shows the  $T_g$ s and  $T_x$ s of boron tellurites with 3, 2, 1, 0.5, and 0 -mol %  $\text{B}_2\text{O}_3$ . By applying a linear fit to the extrapolated data, the  $T_g$  and  $T_x$  of pure amorphous  $\text{TeO}_2$  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  $\text{TeO}_2$   $T_g$  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  $\text{TeO}_2$  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.<sup>4,6</sup> This larger sample size will allow for a greater variety of structural tests to be run.

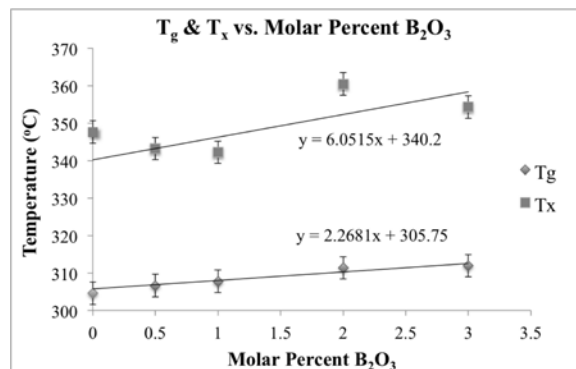


**FIGURE 3.** Overlaid Raman spectra from pure TeO<sub>2</sub> glass and the alpha phase TeO<sub>2</sub> crystal. The glass spectrum has broad peaks, which are indicative of a disordered structure, compared to the sharp peaks of the crystal.

DSC results for pure TeO<sub>2</sub> place the T<sub>g</sub> 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 TeO<sub>2</sub> 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 TeO<sub>2</sub> being approximately 3.7, which is consistent from values found in the literature.<sup>1,5</sup> Looking at the coordination number of pure SiO<sub>2</sub> 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 SiO<sub>2</sub>, TeO<sub>2</sub> 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 TeO<sub>2</sub> 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.<sup>7</sup> For further study of this, gamma phase crystal must be produced by heat-treating small samples of pure

TeO<sub>2</sub> glass, as those are the conditions where this crystal has been formed.<sup>1,7</sup> 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<sub>g</sub>s and T<sub>x</sub>s of doped B<sub>2</sub>O<sub>3</sub> tellurite glasses. The trend extrapolated from this data was used to predict the T<sub>g</sub> of pure amorphous TeO<sub>2</sub>. The measured T<sub>g</sub> and T<sub>x</sub> of pure TeO<sub>2</sub> have since been added.

## ACKNOWLEDGEMENTS

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