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Structure and glass transition temperatures of tellurite glasses

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Tellurite glasses, made from the conditional glass former TeO_2, show potential for use in optical applications. Alkali and alkaline earth tellurite glasses, along with single component, rapidly cooled, TeO_2 are reported and studied here. Thermal properties of boron, potassium, lithium, sodium, rubidium, cesium, barium, and strontium tellurites were obtained via differential scanning calorimetry and related to structural changes observed using Raman spectroscopy. Additionally, coordination numbers of barium and strontium tellurites versus amount of modifier are also calculated. By understanding the thermal properties and coordination numbers of alkali and alkaline earth tellurites, the goal is to better elucidate the structure of amorphous TeO_2.

1. Introduction

Tellurium dioxide (TeO_2) is a conditional glass former and the application of rapid cooling through the twin roller technique has enabled glass formation to a limited extent.[(1)] Modification of tellurium dioxide by the addition of dopants results in much easier glass formation with slower cooling rates and consequently produces higher glass yield. These modified tellurite glasses show potential for use in mid-infrared optical applications,[(1)] but their structure is still not fully understood. While they do have lower refractive indices and a more limited window of transmission in the mid-infrared than chalcogenide glasses, they are much easier to produce.[(1)]

In this paper we seek to extend the understanding of the structure and properties of binary tellurite glasses by reporting on the physical properties and structure of single phase TeO_2 glass and a range of binary boron, sodium, lithium, potassium, rubidium, cesium, barium, and strontium oxide modified tellurite glasses. The physical properties measured were the glass transition temperature (T_g) and the crystallisation temperature (T_x). Raman spectroscopy was employed to infer structural information.

All conventional pure, single phase glasses, such as B_2O_3, SiO_2, P_2O_5, and GeO_2, have an average coordination number that is an integer and, where spectroscopic measurements are available, are shown to be comprised of a single coordination environment,[(2–4)] with a short range glassy structure that is similar to the α-crystal phase.[(5)] Recent results using ^{17}O NMR are consistent with only four coordinated units in amorphous TeO_2.[(6)] Neutron scattering and Raman spectroscopy, however, indicate that this is not the case.[(7)] Instead, it shows a fraction of three coordinated units are also present, as shown in Figure 1. Based on that work, pure TeO_2 glass forms approximately two-thirds four coordinated units and one-third three coordinated units, giving rise to a broad distribution of Te–O bond lengths and asymmetrical bonds.[(7)] The Raman results, in particular, are qualitatively in agreement with the results published by Kalampounias *et al*.[(8)]

2. Experimental Procedures

2.1 Glass preparation

The binary glasses were made by mixing together reagent grade (or better) tellurium dioxide with boric acid, potassium carbonate, lithium carbonate, sodium

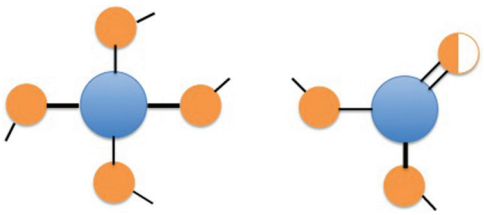

Figure 1. Short range structural units in amorphous tellurium dioxide. Large circles are tellurium and small circles are oxygen. Four coordinated unit is on the left and three coordinated unit is on the right, which includes one double bonded oxygen [Colour available online]

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carbonate, rubidium carbonate, cesium carbonate, barium carbonate, and strontium carbonate. The boron, lithium, sodium, and potassium tellurites and pure TeO_2 glasses were made in 4–10 g well-mixed batches in platinum crucibles. The batches were heated at 800°C for 10 min after which a weight loss was used to check that all CO_2 has been removed. The glasses were then reheated at the same temperature for another 10 min, at which point the samples were quenched into glasses as described below. Barium tellurite and strontium tellurite glasses were made in 10–15 g well mixed batches, heated at 850°C for 20 min after which a weight loss was taken, and the glasses were heated at the same temperature for another 10 min. Alternatively, batches of glass were placed in the furnace at room temperature, ramped up to 350°C, held for 15 min, and then ramped up to 850°C and held for an additional 15 min. Afterwards, a weight loss was taken, and the samples were heated again at 850°C for 15 min. Weight losses for all glasses were consistent with expected CO_2 loss. Glasses were either plate quenched between stainless steel plates (for barium tellurites and strontium tellurites) or roller quenched[9] (for the boron tellurites, alkali tellurites, and pure TeO_2). Crucibles and samples of the 20–30 mol% of $K_2O.TeO_2$ were put into a glove box for the second heating and roller quenching due to the hygroscopicity of the K_2O. All glasses produced were yellow or orange tinted, likely due to small amounts of platinum contamination in the ppm range.[10]

Alternative to the roller quenching method, another procedure for making pure TeO_2 was investigated.[11,12] Roughly 1–1·5 g of 99% purity tellurium dioxide from the Sigma Aldrich Company were measured out in a platinum crucible. The sample was then heated at 1000°C for 10 min. After the 10 min heating, the sample was moved in a circular motion, with a 20 cm diameter, until the liquid in the crucible reached a dark orange colour. Once the sample reached this colour, the crucible was moved in a smaller circular motion of 10 cm until the colour reached yellow orange. Then the bottom of the crucible was quickly dipped into a one litre beaker filled with water at room temperature (~23°C). This water quenching procedure was repeated with a 5 min heating at 1000°C until glass was successfully created. The current success rate with this method is about 75%. This was also the method used to fabricate the rubidium and caesium tellurites in 1–6 g batches.

2.2. Thermal measurements

Thermal measurements using differential scanning calorimetry (DSC) were performed. Pure amorphous TeO_2 and all binary glasses were run on either a TA model Q200 Differential Scanning Calorimeter at 40°C/min or a Perkin Elmer DSC7 Differential Scanning Calorimeter at 10°C/min. Two different DSCs and methods were used because the work in this paper was done at two different universities: Coe College and the University of Nottingham. Similar results were obtained using either method. The onset method was used to determine T_g and T_x.

2.3. Raman measurements

Raman spectra were measured for amorphous TeO_2, the boron tellurite glasses and the alkaline earth glass families. The measurements were carried out using two different instruments. The first was a JASCO NRS-3100 Laser Raman Spectrophotometer with a 785 nm laser, employing a silicon crystal reference for calibration at 520·52 cm^{-1}. For this instrument the sample was focused using a 5×, 20×, and 50× lens successively. The intensity of the laser was optimised to minimise noise. Two 30 s runs were averaged to eliminate cosmic ray events. Raman was also carried out using a LabRAM HR Confocal Raman Microscope with a 659·41 nm wavelength laser.

Raman spectra for pure TeO_2 and barium and strontium tellurites were deconvoluted using the free Fityk software.[13] Fitting was carried out using no fixed parameters and starting values for the four peaks were derived from Sekiya *et al*.[14] The strontium tellurites of compositions 5–20% SrO were made multiple times and Raman spectroscopy was performed repeatedly to provide an average coordination number.

3. Results

Table 1 lists all T_g and T_x results from the glasses studied. Changes in T_g and T_x with composition for the boron tellurite glass family are shown in Figure 2 and the measured T_g values for the alkali tellurite

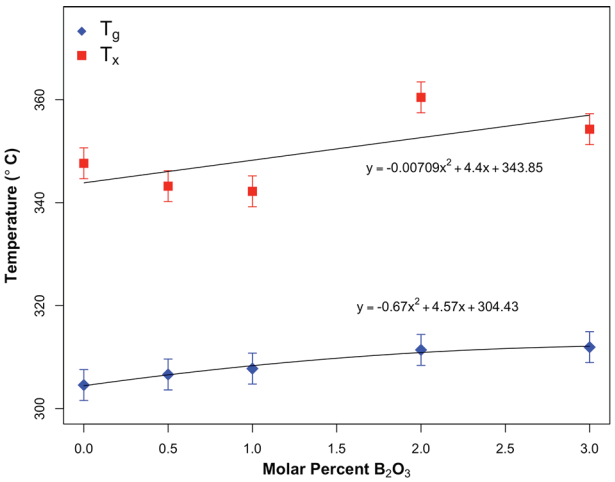

Figure 2. T_g and T_x of boron tellurites which were used to extrapolate the T_g and T_x of pure TeO_2 using polynomial fits. Data points for the pure TeO_2 results have since been added [Colour available online]

Table 1. DSC results for tellurites studied in this paper

Glass	T_g±3 (°C)	T_x±3 (°C)
TeO_2 (yellow tint)	306	348
TeO_2 (orange tint)	310	327
0·01K_2O–0·99TeO_2	304	326
0·02K_2O–0·98TeO_2	302	337
0·03K_2O–0·97TeO_2	302	341
0·05K_2O–0·95TeO_2	297	370
0·10K_2O–0·90TeO_2	282	376
0·15K_2O–0·85TeO_2	262	416
0·20K_2O–0·80TeO_2	240	326
0·25K_2O–0·75TeO_2	221	293
0·30K_2O–0·70TeO_2	205	250
0·05Li_2O–0·95TeO_2	293	347
0·10Li_2O–0·90TeO_2	282	352
0·15Li_2O–0·85TeO_2	270	348
0·20Li_2O–0·80TeO_2	263	368
0·25Li_2O–0·75TeO_2	256	310
0·30Li_2O–0·70TeO_2	250	299
0·05Na_2O–0·95TeO_2	296	335
0·10Na_2O–0·90TeO_2	282	366
0·15Na_2O–0·85TeO_2	268	472
0·20Na_2O–0·80TeO_2	252	434
0·25Na_2O–0·75TeO_2	240	422
0·30Na_2O–0·70TeO_2	227	312
0·005B_2O_2–0·995TeO_2	307	340
0·01B_2O_2–0·99TeO_2	309	344
0·02B_2O_2–0·98TeO_2	311	360
0·03B_2O_2–0·97TeO_2	314	356
0·05BaO–0·95TeO_2	314	
0·10BaO–0·90TeO_2	322	
0·15BaO–0·85TeO_2	330	
0·20BaO–0·80TeO_2	335	
0·25BaO–0·75TeO_2	344	
0·30BaO–0·70TeO_2	355	
0·05SrO–0·95TeO_2	317	
0·10SrO–0·90TeO_2	326	
0·15SrO–0·85TeO_2	338	
0·20SrO–0·80TeO_2	345	

family are shown in Figure 3. In Figure 4, an example DSC trace of glassy TeO_2 is shown. The T_g, given in the inset, was determined to be 305°C, consistent with trends/extrapolations from the sodium and strontium tellurite glasses reported here, other families of doped tellurium glasses that have been studied in the literature,[14] and with a recent report from the Kamitsos group by Tagiaraa *et al*.[11]

Raman spectroscopic results from pure TeO_2 and boron tellurites were first obtained to verify

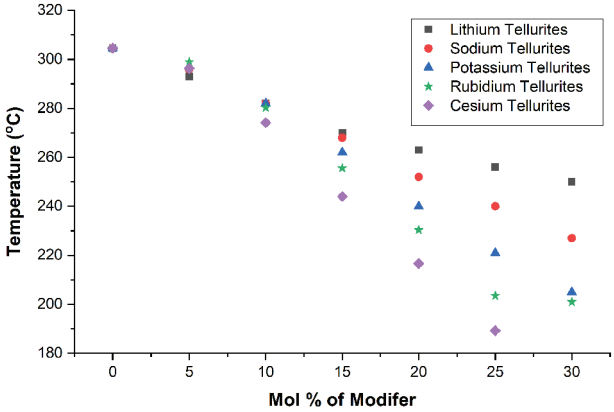

Figure 3. T_g of the alkali tellurite family with 5–30 mol% modifier. The T_g of pure TeO_2 is also plotted [Colour available online]

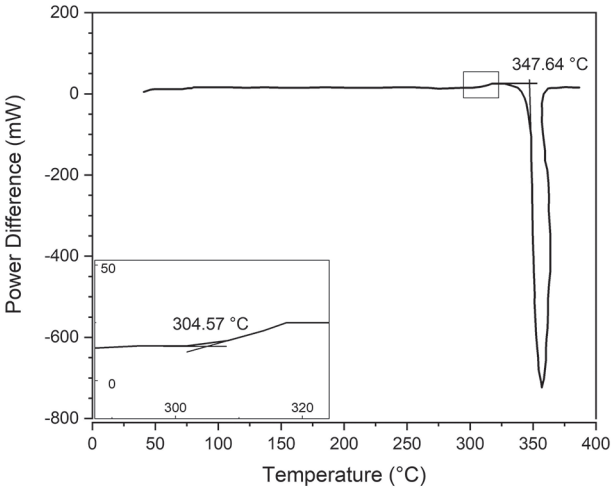

Figure 4. DSC output for amorphous TeO_2. 305±3 °C is the measured T_g and 348±3 °C is the measured T_x

glassiness. For the boron tellurites, 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 for the doped samples were compared to the pure TeO_2 sample. No discernable difference was noticed between them; all were glassy and similar to the broad spectrum in Figure 5, which shows spectral differences for pure TeO_2 glass and the alpha phase TeO_2 crystal. The peaks of the crystal spectrum are sharp, which we would expect, and the glass peaks are broader, which is indicative of a disordered structure.

The spectra measured for the alkaline earth samples was used to verify glassiness and then fitted to find an estimation of the coordination number. An example fit to the 10 mol% BaO.TeO_2 glass is shown in Figure 6. The resultant widths and peak positions of Raman spectra deconvolutions are listed in Tables 2–3. Coordination numbers were averaged from these spectra and are represented in Figures 8–9.

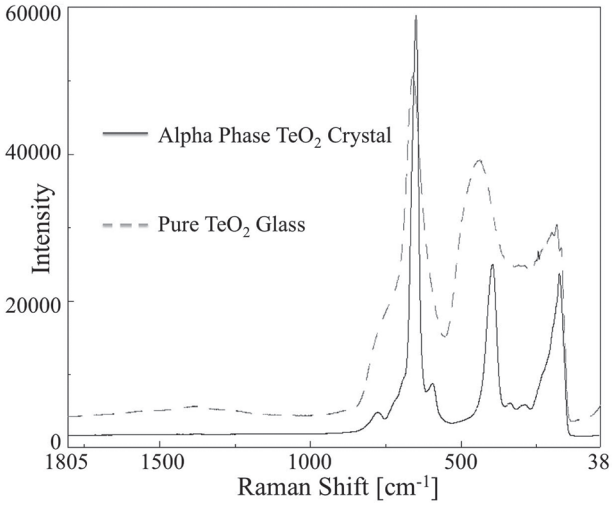

Figure 5. Raman spectra of amorphous TeO_2 glass and the α-phase TeO_2 crystal

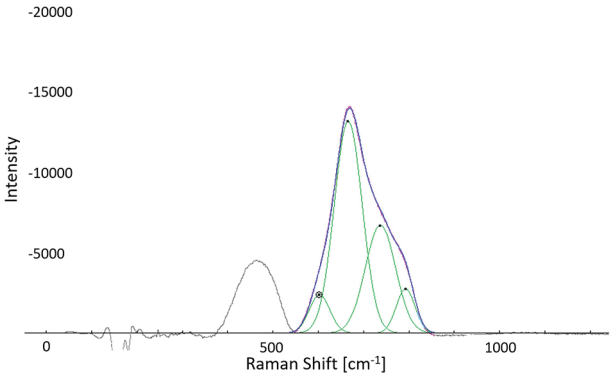

Figure 6. 10 mol % BaO.TeO_2 fit showing the deconvolved peak positions. The two peaks on the left correspond to four coordinated units while the right two peaks are three coordinated. X-axis is Raman shift [cm^{-1}] and the y-axis is intensity [Colour available online]

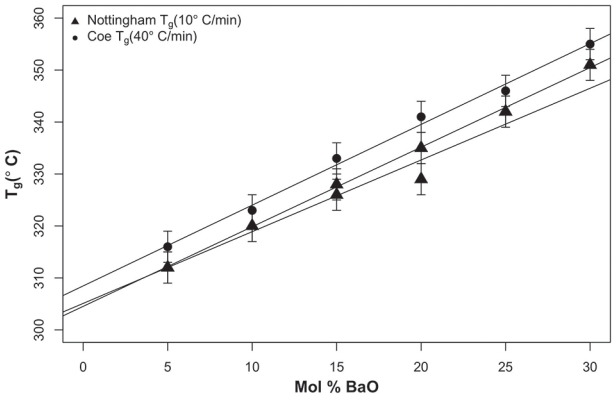

Figure 7. The T_g of barium tellurite glasses with a linear trend estimating the T_g of pure TeO_2. Results were obtained using two different DSCs and ramp rates as described in the thermal measurements section

4. Analysis and discussion

4.1. DSC Data

Figure 4 shows the T_g and T_x of the boron tellurite glasses. By applying a polynomial fit to the data, the T_g and T_x of pure amorphous TeO_2 are estimated to be around 306±3°C and 340±3°C, respectively. The T_g extrapolated was within in error to the measured TeO_2 T_g of 305±3°C, while the T_x was slightly farther off from that of TeO_2 glass, 348±3°C, as seen in Figure 2. The glass stability equals $T_x - T_g$=43°C, a small value, meaning that a very high cooling rates must be achieved for glass to form.

The alkali tellurite family consisting of potassium, lithium, sodium, rubidium, and caesium tellurites was also studied, extending out to compositions of 30 mol% modifier. Unlike the boron and alkaline earth tellurites, the T_g plotted in Figure 5 decrease with the addition of a modifier. This reduction is likely due to the formation of nonbridging oxygen (NBO) on the Te unit. The T_g of the alkali tellurites differ by about 20°C at 30 mol% but all converge on the 305±3°C point as the amount of modifier is reduced.

Figure 7 is a plot of various T_g results of glassy barium tellurites. The trend of the T_g increases as modifier is added. Each trend also extrapolates to the known T_g of pure TeO_2 glass of 305±3°C. Crosslinking of Ba^{+2} has been shown in other glass systems to cause an increase in T_g.[15]

Table 2. Barium tellurite Raman deconvolution data

Composition	*Average centre (cm^{-1})*	*Average FWHM (cm^{-1})*	*Coordination number, x*	*Fraction TeO_x*	*Average CN*
0·00 BaO	782	62	3		
	712	97	3	0·41	
	661	45	4		
	621	63	4	0·59	3·59
0·05 BaO	786	55	3		
	724	82	3	0·40	
	661	56	4		
	610	55	4	0·60	3·6
0·10 BaO	788	51	3		
	731	75	3	0·41	
	663	68	4		
	603	56	4	0·59	3·59
0·15 BaO	790	49	3		
	734	77	3	0·48	
	662	74	4		
	600	53	4	0·52	3·52
0·20 BaO	791	47	3		
	738	79	3	0·55	
	660	77	4		
	597	53	4	0·45	3·45
0·25 BaO	789	45	3		
	744	70	3	0·56	
	664	83	4		
	595	50	4	0·44	3·44
0·30 BaO	793	35	3		
	761	68	3	0·54	
	671	101	4		
	584	34	4	0·46	3·46

4.2. Raman spectra

The proposed structure is composed of two arrangements: three and four coordinated TeO_2.[7] Raman

Table 3. Strontium tellurite Raman deconvolution data

Composition	*Average centee (cm^{-1})*	*Average FWHM (cm^{-1})*	*Coordination number, x*	*Fraction TeO_x*	*Average CN*
0·00 SrO	782	62	3		
	712	97	3	0·41	
	661	45	4		
	621	63	4	0·59	3·59
0·05 SrO	783	58	3		
	716	90	3	0·42	
	657	59	4		
	605	57	4	0·58	3·58
0·10 SrO	791	56	3		
	729	84	3	0·50	
	660	69	4		
	601	52	4	0·50	3·50
0·15 SrO	795	51	3		
	737	86	3	0·51	
	658	79	4		
	593	46	4	0·49	3·49
0·20 SrO	799	45	3		
	748	81	3	0·60	
	661	89	4		
	588	46	4	0·40	3·43

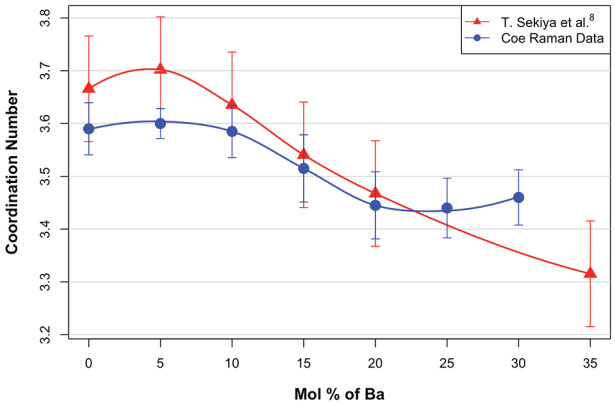

Figure 8. Coordination number of barium tellurites [Colour available online]

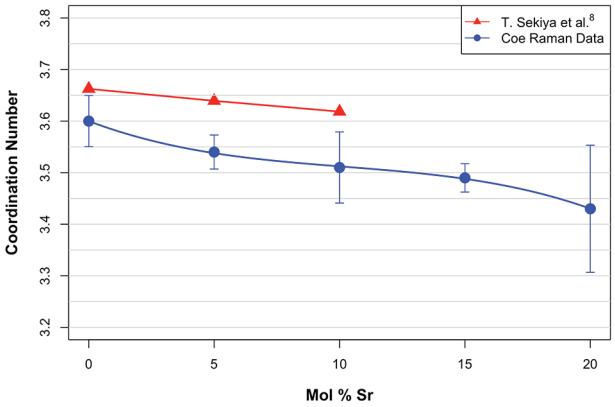

Figure 9. Coordination number of strontium tellurites [Colour available online]

deconvolutions were obtained using gaussian fitting by the software Fityk;[13] the numerical results are shown in Tables 2–3. Four different peaks were used; the two peaks around 700 cm^{-1} arise from three coordinated Te and the two peaks around 600 cm^{-1} are from four coordinated Te.[7] The coordination numbers were determined by the relative areas of the 700 cm^{-1} and 600 cm^{-1} peaks, respectively. To get the specific or sample average coordination number, the fraction of three and four coordinated Te units were multiplied by three and four respectively and then added together.

The coordination number versus molar percent of the alkaline earth tellurites were calculated and are given in Figures 8–9 (for Ba and Sr). The different trends are from the present deconvolution and Sekiya *et al*.[14] The coordination numbers decrease as we add more modifier.

5. Conclusions

While it is possible to produce small amounts of pure TeO_2 glass via the roller quenching technique, it is not a feasible method for large-scale fabrication. Instead, a water quenching technique has recently been used to create from 0·6 up to 3 g samples.[11,12] This larger sample size will allow for a greater variety of structural tests to be run.

DSC results for pure TeO_2 place the T_g at approximately 305°C, which is consistent with the extrapolation of trends from the families of borate, alkali, barium, and strontium tellurites and other literature values.[7] In addition to thermal measurements, coordination numbers of TeO_2 for the barium and strontium tellurite systems were calculated from Raman data. 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 nonbridging oxygens in the tellurite system. The strontium tellurite system shows a similar behaviour. The most interesting result to notice, however, is that the trends of both families point to the coordination number of pure TeO_2 being approximately 3·6–3·7, which is consistent with our measurement of glassy TeO_2 and most values found in the literature.[8,14] Looking at the coordination number of pure SiO_2 glass, which is 4, this could explain why pure TeO_2 glass is so difficult to produce in large quantities. Instead of having an even number of similarly sized bonds, as in SiO_2, TeO_2 most likely has bonds that are asymmetrical in length, thus making a cohesive short range order harder to achieve. On the other, hand a recent ^{17}O NMR study indicates that TeO_2 is four coordinated and another recent NMR results gives the coordination of about 3·9.[6,16] More work needs to be done to properly characterise the structural nature of pure amorphous TeO_2.

One possible route is to use the γ-phase crystal of TeO_2, as preliminary work suggests it matches the structure of the amorphous glass better than the α-phase crystal.[17] For further study of this, γ-phase crystal must be produced by heat treating small samples of pure TeO_2 glass, as those are the conditions where this crystal has been formed.[7,17] Work will also continue in the alkaline earth tellurite families by roller quenching the calcium and magnesium tellurite systems.

Acknowledgements

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