A Wide-Angle X-ray Diffraction Study of Alkali Tellurite Glasses

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Introduction

Alkali tellurite glasses ($M_2O \cdot TeO_2$, with $M = Li, Na, K$) are of current interest in technology, as components of optically nonlinear materials, and fundamentally, due to the unusual glass forming properties of tellurium dioxide (TeO_2). This oxide is four-coordinate but nevertheless only a conditional glass former; addition of alkali oxides gives rise to ranges of excellent glass formation, and in fact enhanced stability against devitrification at about the 20 mol% alkali oxide composition [1]. The optical properties arise from the polarizable lone pair of electrons carried by each tellurium atom [2]. Understanding the structure of these glasses and its relation to their properties is important in their use, and is the subject of the present experiment.

The structural study of such materials requires multiple probes, because of their complex and amorphous nature. Our program uses x-ray and neutron diffraction along with NMR and Raman spectroscopies to generate a broad range of structural data. The APS is particularly suitable as an x-ray source for this study, because the experiment requires both high count rates and moderately high photon energies. The latter requirement arises from the need to avoid sample absorption, and to collect data out to large momentum transfer. Here we discuss how the x-ray diffraction portion of this work is performed, and how the results it provides are used to make models of alkali tellurite glasses (see also [3]).

Methods and Materials

Samples of tellurite glasses were prepared by melting alkali carbonates and tellurite together at 800°C for 15 minutes. Glasses of composition $(M_2O)_x(TeO_2)_{1-x}$ with $0.1 < x < 0.3$ and $M = Li, Na, K$ were prepared for this study. The liquids were quenched between steel or brass plates, and thus formed as plates of about 0.5 mm thickness. Sample composition was determined by weight-loss measurements and in some cases by electron microprobe analysis. The final compositions are precise to within $\pm 1\%$. The glass transition temperatures were found by differential scanning calorimetry and agreed within experimental error with previously published data [1].

X-ray diffraction was performed on the Sector 1 bend-magnet beamline (1-BM), operated by the Synchrotron Research and Instrumentation Collaborative Access Team (SRI-CAT) at the Advanced Photon Source, Argonne National Laboratory. 61.332 keV photons were used in order to be well above all
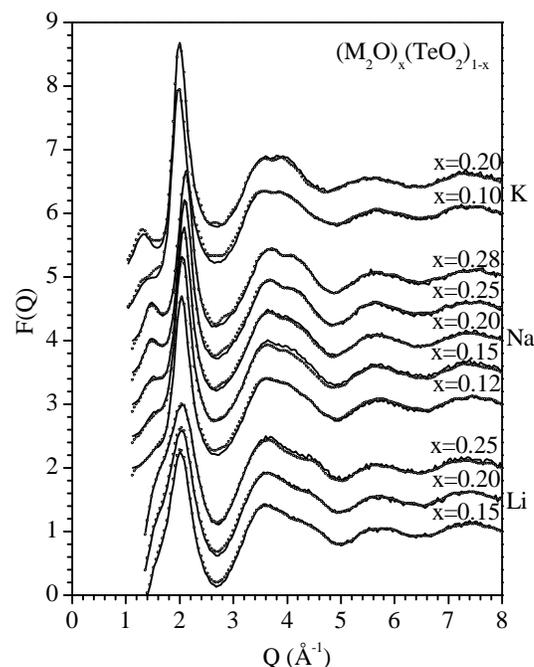

Figure 1: Total structure factors $F(Q)$ for all glasses studied. The data has been corrected for instrumental artifacts, normalized, and incoherent scattering has been removed as detailed in the text.

absorption resonances, achieve wide Q-space coverage, and yield predominantly interior rather than surface diffraction. The photons were selected with a single Si (111) crystal with a 1.6° miscut. The crystal was bent (meridionally) to a monochromatic focus at the detector position. The monochromator crystal deflection was horizontal, while the scattering plane for the sample/detector was vertical in order to preserve acceptable angular resolution. A Ge solid-state detector was used. The thin plate samples were mounted and studied in transmission mode. They were scanned through θ as the detector was scanned through 2θ. The structure factor, $F(Q)$, was extracted from the raw diffraction data, by correcting for Compton scattering, absorption, polarization, and background diffraction, following the procedure outlined by Williams [4]. The instrument dead-time was also measured and compensated for in the data analysis.

Results

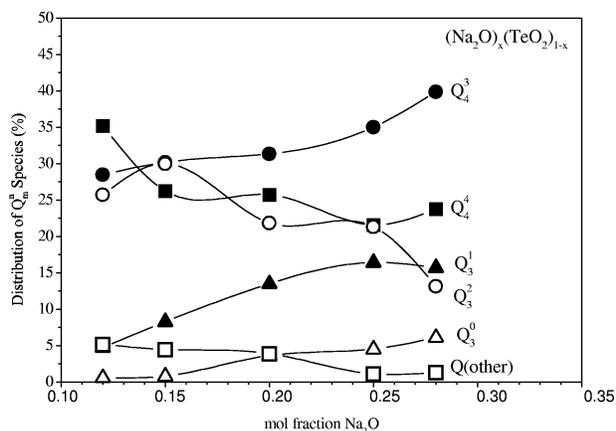The key quantity in this work is the total structure factor,

Figure 2: Distributions of tellurite polyhedral types as a function of sodium oxide, for sodium tellurite glasses. These results were obtained by modeling combined data sets from x-ray and neutron diffraction and NMR. The Q_m^n symbols indicate tellurium with m bound oxygen, n of which are bridging.

corrected as described above for incoherent scattering and experimental artifacts. The data so processed is shown in Figure 1.

Discussion

From the data shown in Figure 1, together with complementary experiments including neutron diffraction and NMR, models of the glass structure can be constructed using the Reverse Monte Carlo algorithm [5]. Figure 1 in fact also shows fits to the data, based on real space models made in this way. The most important quantities that the models yield are the distributions of tellurium oxide polyhedral types. The polyhedral types are denoted Q_m^n, where m denotes the number of oxygen bound to the tellurium, and n the number of these oxygen which form bridges to other tellurium atoms. Our previous crystallographic studies showed that 5 species are found in crystalline forms: Q_4^4 and Q_4^3, and Q_3^2, Q_3^1, and Q_3^0. These are in fact all possible types consistent with oxidation state $+4$ for the tellurium.

Figure 2 shows a graph of the different Q_m^n species, consistent with the diffraction data shown in Figure 1 and also neutron and NMR experiments (data not shown), for the specific case of Na$_2$O. As the mol-% Na$_2$O increases, groups of lower coordination number appear at the expense of those with higher, indicating that the network is progressively cleaved. The original crystalline TeO$_2$ network is composed of TeO$_4$ trigonal bipyramids (Q_4^4). The fraction of tellurium atoms in Q_4^4 groups steadily decreases from about 40 to 20 % as the mol-% Na$_2$O increases. The Q_4^3 and Q_3^2 polyhedra, which maintain network connectivity while still possessing one non-bridging oxygen, together decrease steadily from

about 35 to 25 %. The Q_3^1 and Q_3^0 groups reflect the breaking of the TeO$_2$ network, as they result in a terminating group or a lone TeO$_3^{2-}$ group respectively. Based on the data for the Q_m^3 groups we suggest an underlying chemical equilibrium attained in the melt prior to quenching.

We find that all five tellurite polyhedra are necessary to obtain models consistent with the full data sets presented here. For example, if the Q_3^2 unit is explicitly rejected, while all other units are permitted, even limited ranges of the neutron and x-ray diffraction data cannot be fit. However, if only the x-ray or neutron data sets are used, a reduced set of polyhedra is sufficient to obtain a fit. This finding indicates that any single data set, even of diffraction, can be expected to yield an incomplete picture of the structure of a multi-component glass.

Conclusions

Understanding and developing the properties of amorphous solids requires complete structural characterization, and thus for multi-component systems a range of techniques must be employed. X-ray diffraction is an important tool in such a study, and we have shown in this project how it may be carried out effectively at the APS. The resulting data, together with complementary data from sources such as neutron diffraction and NMR, allow for the characterization of even complex distributions of polyhedral types in a glass, as shown here on alkali tellurite glasses.

Acknowledgments

References

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