Appendix A

DEBYE-GRÜNEISEN THERMAL EXPANSION EFFECT OF $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$

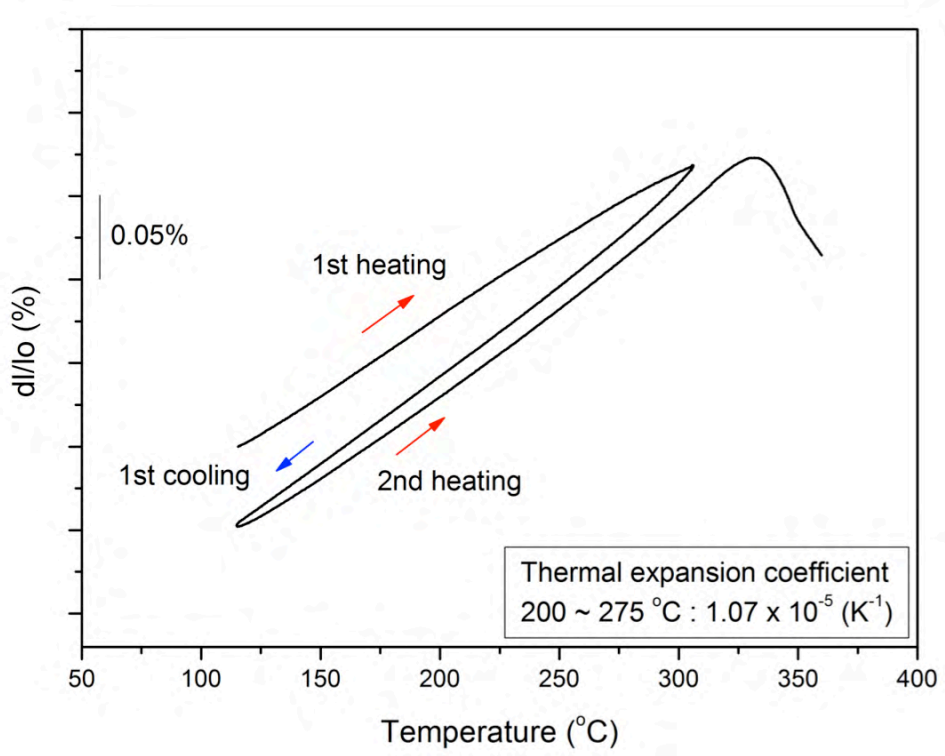

Figure A.1 The linear coefficient of thermal expansion α_{lin} of $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ was determined to be 1.07×10^{-5} K^{-1} between 200 °C and 275 °C using a Perkin Elmer thermomechanical analyzer. The volumetric coefficient of thermal expansion α_{vol} is equal to $3 \cdot \alpha_{lin}$, which is 3.21×10^{-5} K^{-1}. We use α_{vol}, which is basically the change in the volume of the glass with change in temperature, to calculate a temperature-dependent density for the glass. This $\rho(T)$ is used in the calculation of the temperature-dependent elastic modulii, shown in figures A.2 and A.3. The change in density is small but gives a more accurate description of the change in vibrational modes with temperature.

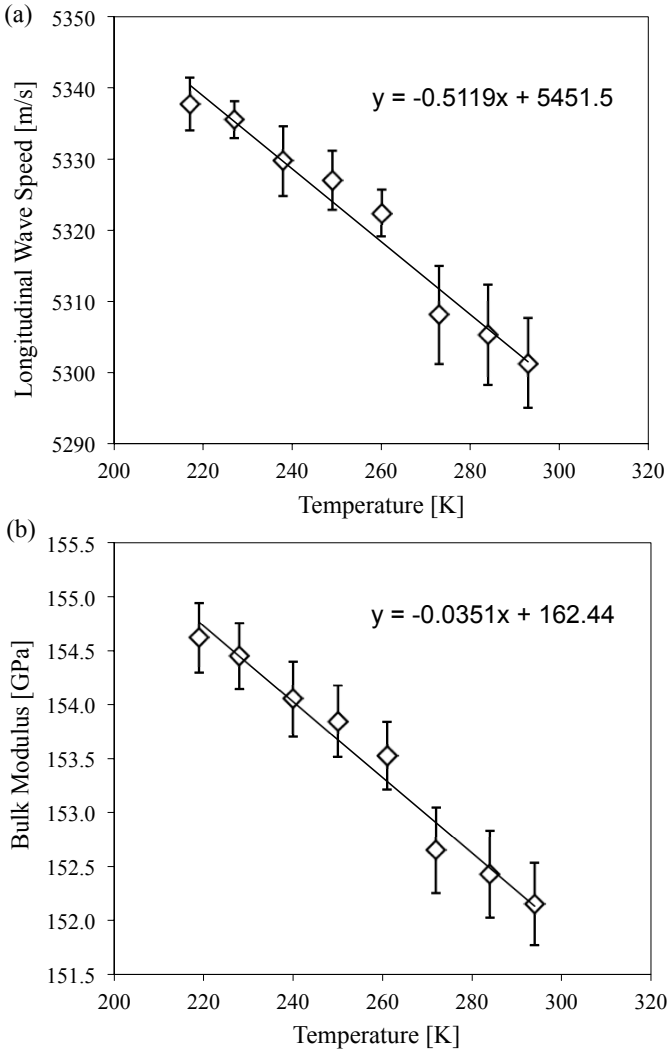

Figure A.2 The longitudinal wave speed (a) of $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ was measured in-situ using a 25 MHz ultrasonic transducer with a long quartz delay line. The sample was cooled using a mixture of dry ice and ethanol between the temperatures of 220 K and 295 K. The bulk modulus (b) was calculated from the longitudinal wave speed and $\rho(T)$. The vibrational change in B with temperature for $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ glass is –35.1 MPa·K^{-1}, and the configurational change in G with temperature determined by ex-situ annealing in chapter 3 is –5.9 MPa·K^{-1}. Thus, the Debye-Grüneisen corrected configurational change in B with T is –41.0 MPa·K^{-1}.

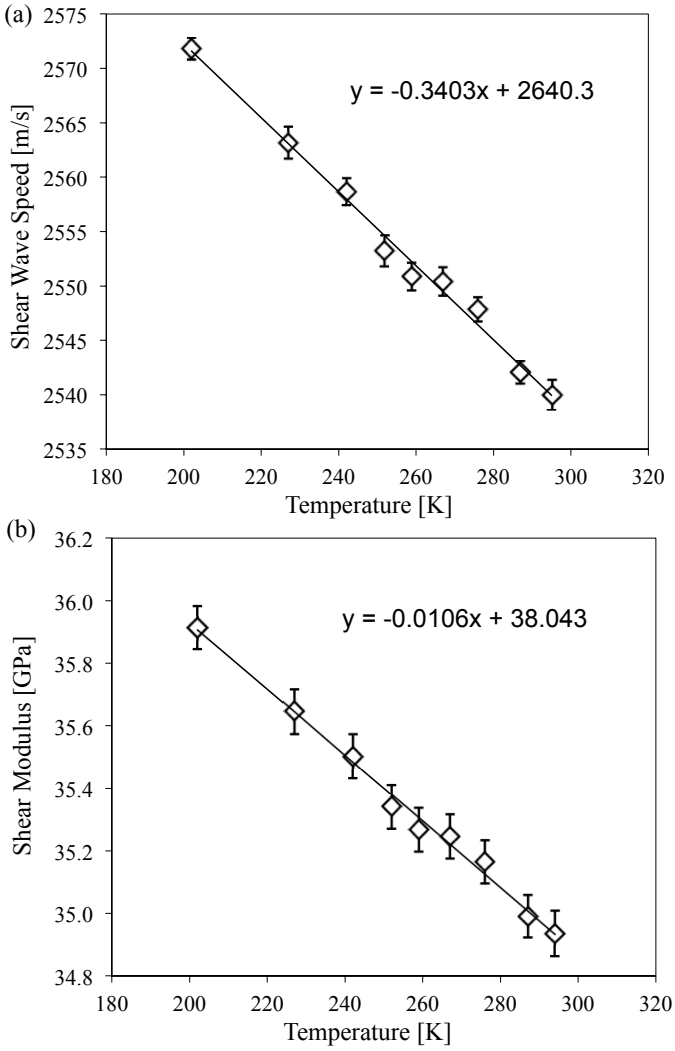

Figure A.3 The shear wave speed (a) of $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ was measured in-situ using a 25 MHz ultrasonic transducer with a long quartz delay line. The sample was cooled using a mixture of dry ice and ethanol between the temperatures of 220 K and 295 K, liquid nitrogen was used for the measurement at 200 K. The shear modulus (b) was calculated from the shear wave speed and $\rho(T)$. The vibrational change in G with temperature for $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ glass is –10.6 MPa·K⁻1, and the configurational change in G with temperature determined by ex-situ annealing in chapter 3 is –23.1 $MPa \cdot K^{-1}$. Thus, the Debye-Grüneisen corrected configurational change in G with T is –33.7 $MPa \cdot K^{-1}$.

Appendix B

BULK MODULUS, POISSON RATIO, AND FRACTURE TOUGHNESS OF $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$

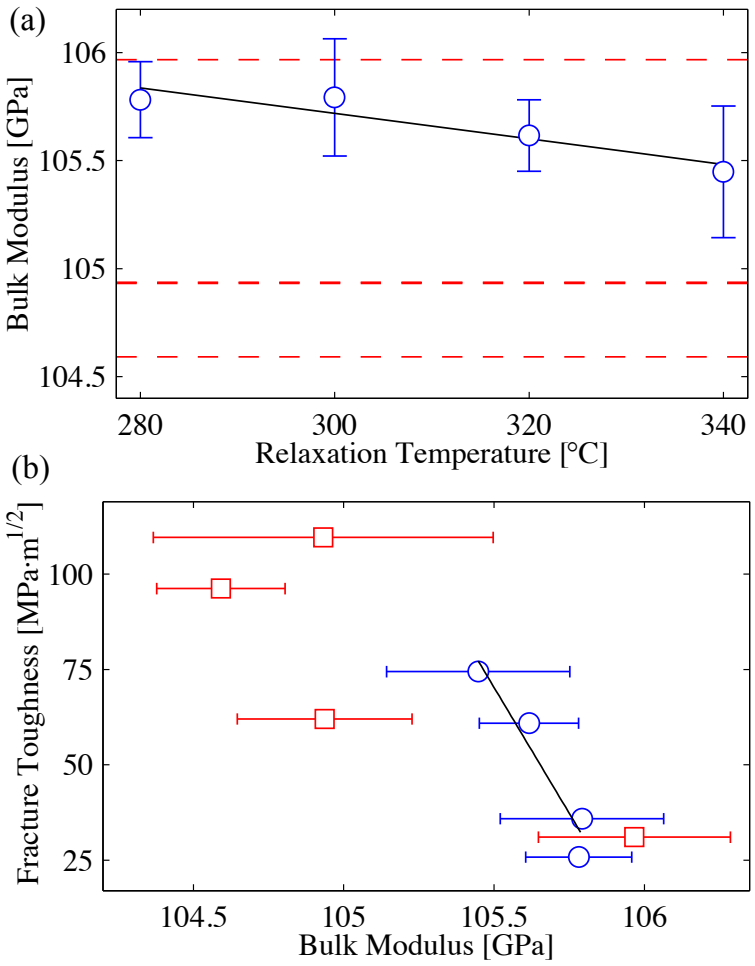

Figure B.1 The bulk modulus of the $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ fracture toughness specimens is plotted against the (a) relaxation temperature and the (b) fracture toughness. The red dashed lines in (a) are the B values for the as-quenched samples and the blue circles are for the relaxed samples. The linear fit to B vs. T_R for the relaxed samples is $-5.9\ \mathrm{MPa \cdot K^{-1}}$. The red squares in (b) are for the as-quenched samples and the blue circles are for the

relaxed samples. The linear fit to K_Q vs. B for the relaxed samples is –132 MPa·m$^{1/2}$·GPa^{-1}, but we must note that the error bars for all of the B measurements are quite large compared to the change in B seen between samples.

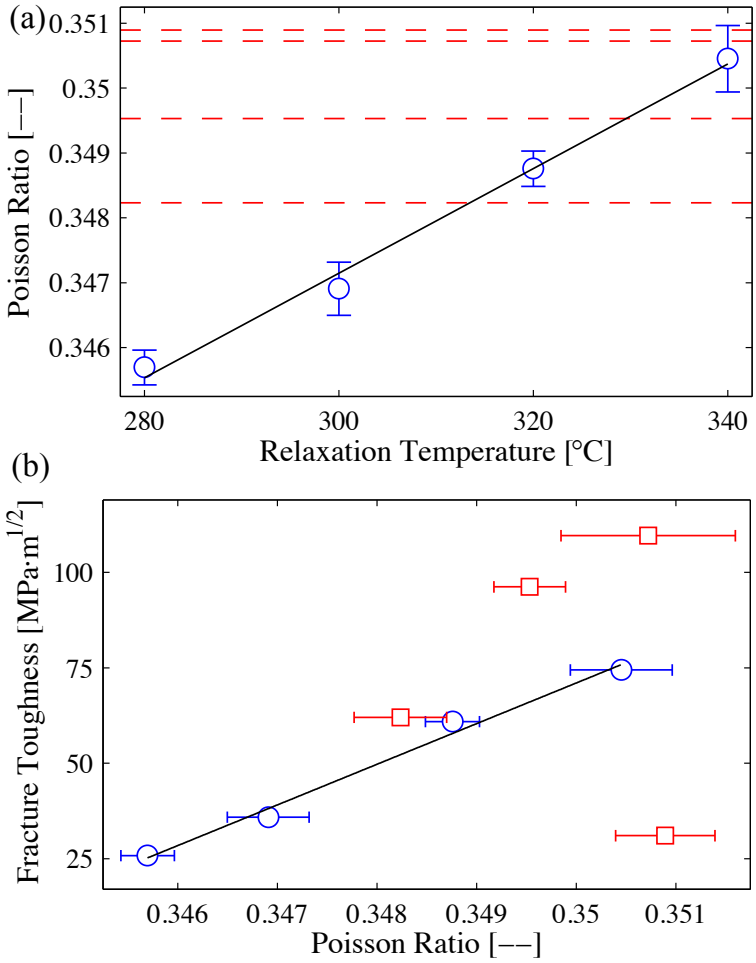

Figure B.2 The Poisson ratio of the $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$ fracture toughness specimens is plotted against the (a) relaxation temperature and the (b) fracture toughness. The red dashed lines in (a) are the υ values for the as-quenched samples and the blue circles are for the relaxed samples. The linear fit to υ vs. T_R for the relaxed samples is 0.000081 K^{-1}. The red squares in (b) are for the as-quenched samples and the blue circles are for the relaxed

samples. The linear fit to K_Q vs. υ for the relaxed samples is 10,644 MPa·m$^{1/2}$, which is easier to understand as a 10.6 MPa·m$^{1/2}$ improvement in toughness for every 0.001 the Poisson ratio is raised. This 0.001 increase in the Poisson ratio corresponds to an increase in the relaxation temperature of 12.3 K, and if we compare this to the fracture toughness we see that for every 10 K the relaxation temperature is increased we raise the fracture toughness by 8.6 MPa·m$^{1/2}$.

Appendix C

DETERMINATION OF ENTHALPY RECOVERY BY DIFFERENTIAL SCANNING CALORIMETRY FOR $Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$

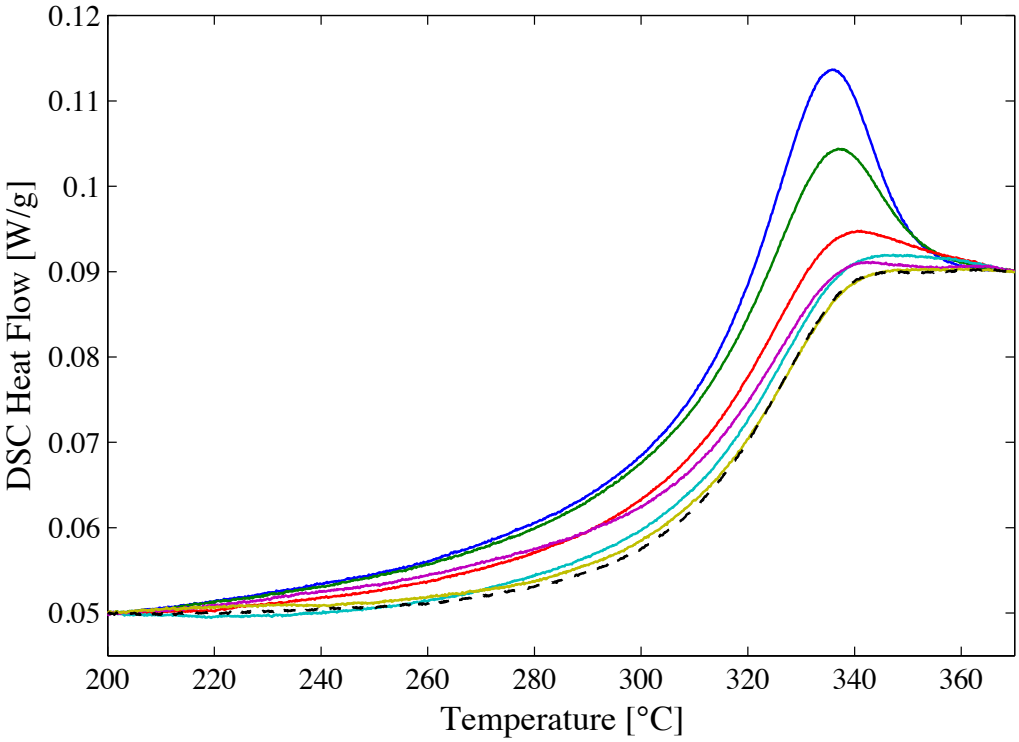

Figure C.1 The differential scanning calorimetry (DSC) scans for all of the fracture toughness specimens are shown above. The scans were performed using a Netzsch 404C calorimeter at a scan rate of 0.16 °C·s^{-1}. Each scan was performed with a baseline and sapphire standard, but the heat capacity of the low temperature glass and liquid above T_g do not line up perfectly for every run. A linear fit was used between 200 °C and 370 °C to normalize the data for comparison. The recovered enthalpies were calculated by integrating each DSC scan between 200 °C and 370 °C, dividing that integral quantity by

the heating rate and molar mass to obtain a J/mol quantity. The recovered enthalpies were then subtracted by the sample that displayed the lowest recovered enthalpy (black dashed line) so that just the relative differences in the recovered enthalpy remain. The resulting ΔH values are listed in table 3.1 and shown vs. relaxation temperature in figure 3.1(b). The samples relaxed to 280 °C (blue line) and 300 °C (green line) have the greatest enthalpy recovered upon passing through T_g, and thus are easily spotted as the scans with tall peaks at ~330 °C in the figure above.