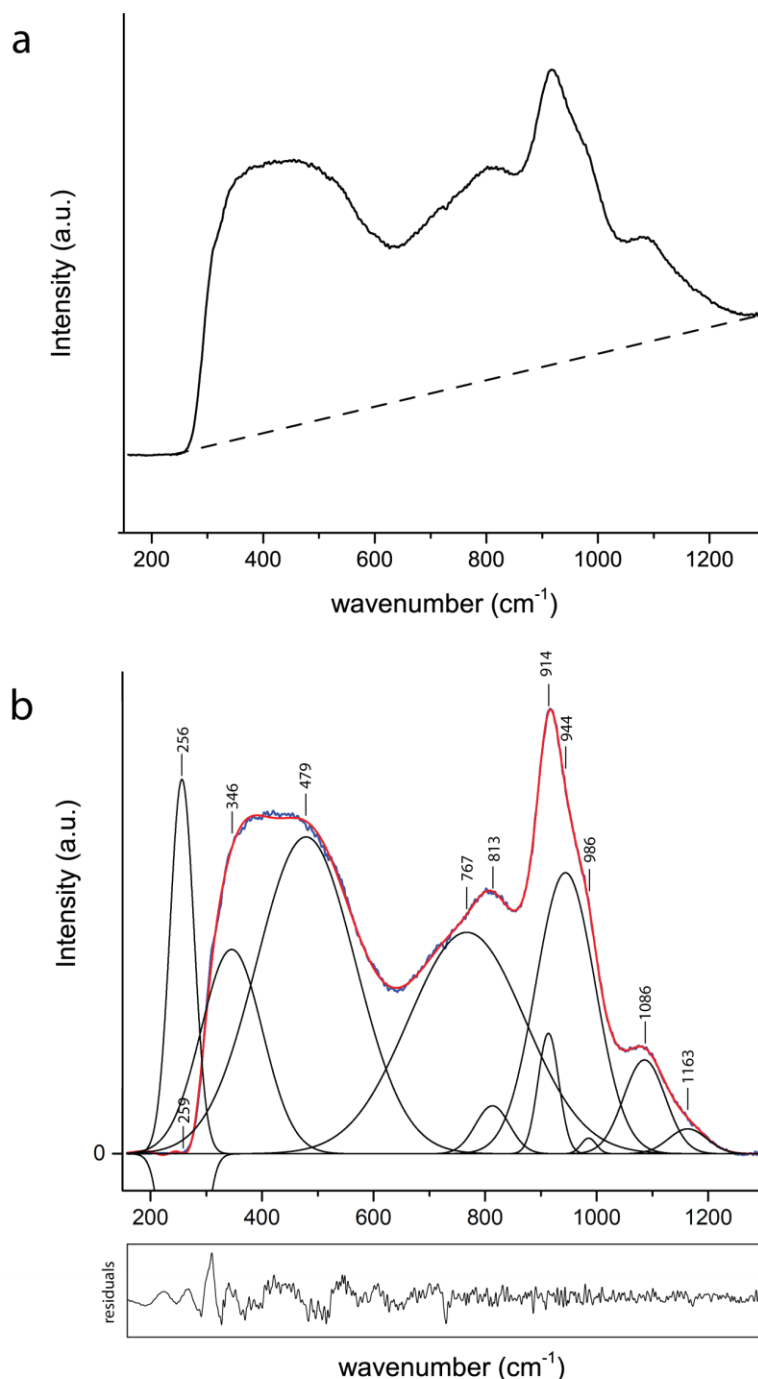


Supplementary Figure S1: XRD spectra of selected experiments overlain with simplified spectra of tridymite (blue) anatase (red) and rutile (green). (a) Ti20NS8 glass quenched from above the solidus is completely amorphous. Background-subtracted spectra for (b) the Ti20NS8 bulk composition crystallized at 1010 °C and (c) the Ti15NS8 bulk composition at 1250 °C. Tridymite and rutile observed optically and in the SEM for the sub-liquidus Ti20NS8 composition are also observed in the XRD spectrum, whereas rutile is absent from the Ti15NS8 composition for which tridymite was the only crystalline phase observed in the SEM. No cryptocrystalline anatase was observed in any experiment.



Supplementary Figure S2: Background subtraction and peak analysis of Raman spectrum from Ti10NS8 glass synthesized at 1400 °C. (a) Raw Raman spectrum with a linear background denoted in dashed line from 370  $\text{cm}^{-1}$  to 1260  $\text{cm}^{-1}$ . Below 370  $\text{cm}^{-1}$  and above 1260  $\text{cm}^{-1}$ , spectra were background corrected to set all values to  $\sim 0$ . (b) One possible fit to the Raman spectrum, performed using Fityk. The background subtracted data (blue) and model (red) are shown with the Gaussian peaks (black) used to create the model. The peaks at 256 and 259  $\text{cm}^{-1}$  are non-real peaks added due to the loss of signal due to the notch filter. See text for details regarding the assignments of other peaks and their relationship to the structure of Ti in the Na-silicate glasses.