Experimental report

31/08/2022

Proposal: INTER-562 **Council:** 4/2021

Title: structure of aluminosilicateglasses by NDIS

Research area:

This proposal is a new proposal

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Samples: (MgO)0.6(AI2O3)0.1(SiO2)0.6(Li2O)x(SiO2)1-x x=0.29,0.33,0.36 with natMg, 25Mg, 7Li, natLi, TiO2-Nb2O5-P2O5

Instrument	Requested days	Allocated days	From	To
D4	7	7	06/09/2021	13/09/2021

Abstract:

Experimental report for proposal INTER-562

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August 31, 2022

1 Summary

Experiments were carried out at the D4c diffractometer at the ILL with the collaboration of Philip Stephen SALMON, Anita ZEIDLER, Hesameddin MOHAMMADI, Gabriel CUELLO (local contact), Federico Hector COVA, Gavin VAUGHAN and Esther GIRÓN LANGE in September 2021. The neutron beam had dimensions of 12 mm and 50 mm of width and height, respectively. A Rh filter was used to suppress $\lambda/2$ contamination and a copper monochromator oriented for Cu(220) reflections selected a wavelength of 0.49777 Å. A standard sample was measured to normalise to absolute units the measurements. This standard was chosen to be a vanadium cylinder of diameter 6.08 mm, height equal to the beam height and a density of 6.51 g/cm^3. Vanadium was chosen because of its small coherent scattering length $b_{\mathrm{V}} = -0.3824(12)$ fm and large incoherent scattering length of $b_{\mathrm{V},inc} = 6.36(4)$ fm. A nickel standard was used to determine the zero-angle offset of the instrument of 0.045972°.

The samples were measured at ambient conditions of temperature and pressure inside a cylindrical vanadium can 60.0 mm tall with 5.0 mm of outer diameter and wall thickness of 0.1 mm. The glasses were ground using an agate mortar and pestle to maximise the amount of sample within the beam. Additionally, the cylindrical geometry of this container facilitates the calculation of the attenuation and absorption corrections. The samples in their containers were loaded inside the evacuated belljar of the instrument.

2 TiO_2-NbO_2-P_2O_5 glass system

Three samples of different Ti, Nb and P concentrations were measured. The samples were prepared at Corning Inc. by Aitken [1]. Table 1 shows the composition of the three samples together with their measured density and packing density inside the can at the time of the experiments. Figure 1(a) shows the raw data measured for the empty

Sample	TiO_2 %	Nb_2O_5 %	P_2O_5 %	ρ[g/cm^3]	ρ_{pack} [g/cm^3]	n [atoms/cm^3]
TNP4035	40	35	25	3.70(8)	1.975(6)	0.0751(4)
TNP5520	55	20	25	3.46(9)	1.885(8)	0.0756(4)
TNP6510	65	10	25	3.30(3)	1.564(5)	0.0767(8)

Table 1: Characterization of the TNP samples giving: the name, the composition, the density (ρ), the packing density (ρ_{pack}) of sample inside the vanadium can for the experiments and its number density (n).

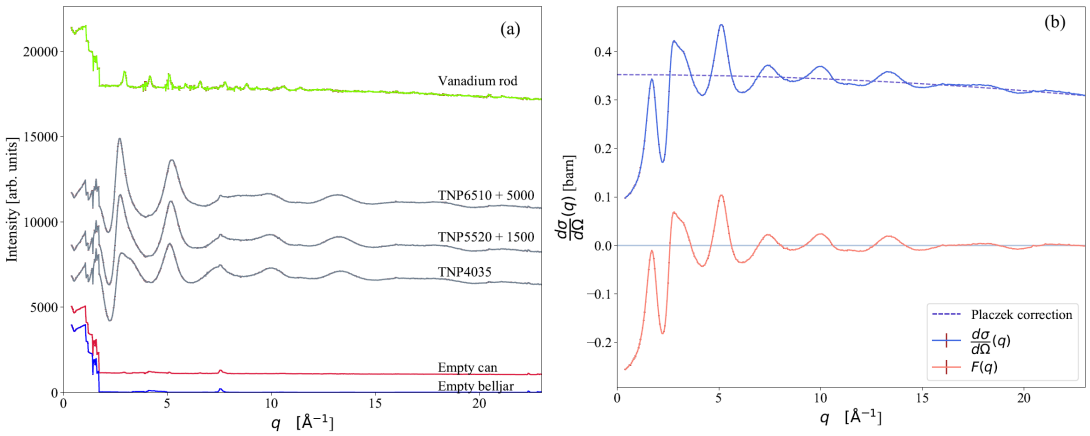

Figure 1: (a) Raw data from the vanadium rod, the empty instrument, the empty can and the three TNP samples. The data for the TNP5520 and TNP6510 has been shifted up for visualization purposes but both oscillate around the same intensity level as the TNP4035 sample. (b) TNP4035 sample corrected for (top) background, attenuation and multiple scattering and (bottom) Placzek. All data is plotted with its corresponding errorbars that are however too small to be visible at this scale.

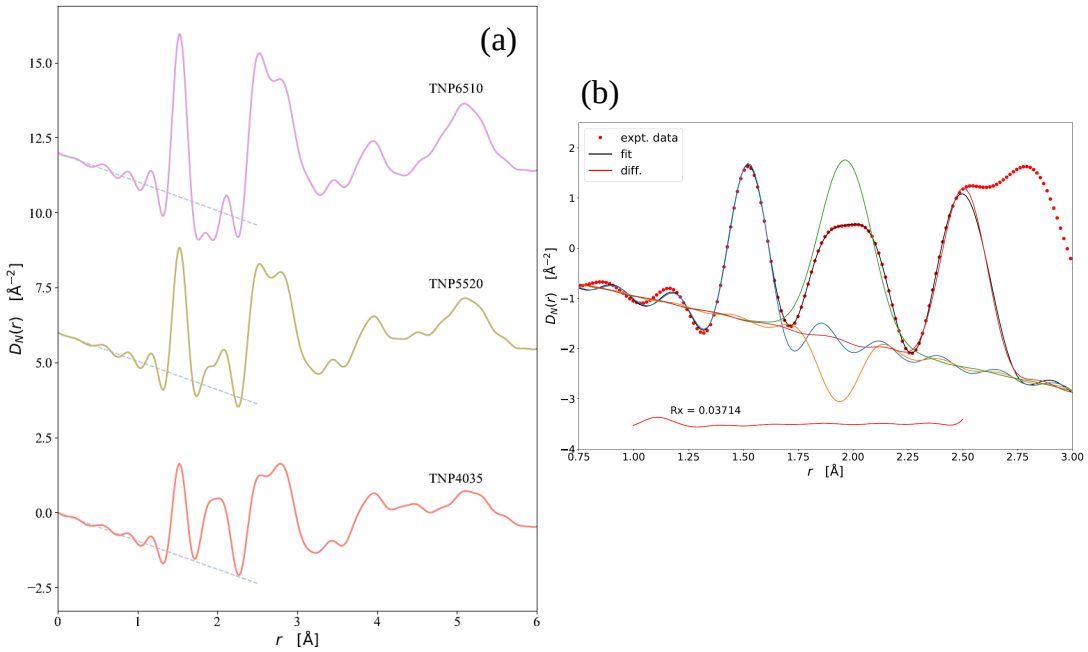

Figure 2: (a)D(r) for all TNP samples obtained by performing the Fourier transform of their total structure factors. Consistency check were done to examine the accuracy of the data corrections. (b) Fit of the TNP4035 $D(r)$ by Gaussian functions. The red dots correspond to the original data while the solid colour lines represent each of the Gaussians used to fit the $D(r)$ function. The peaks used for the fit come from the P-O correlation (blue line), the Ti-O (orange), the Nb-O (green) and O-O (red). The red curve on the bottom shows the residual over the fitted range..

instrument, empty container, vanadium rod and the three TNP samples loaded in the container. The background subtracted is the sum of the empty instrument and the empty container while the measurement of the vanadium rod was used for normalisation purposes. The correction of the data for the three samples was performed following the same procedure but only the TNP4035 is shown hereafter for simplicity.

The raw data were processed using in-house software that subtracts the background, normalises to the vanadium standard, applies multiple scattering corrections and subtracts the empty container from the sample-in-container data using attenuation factors. After these corrections are applied, the differential scattering cross section $\frac{d\sigma}{d\Omega}(q)$ was obtained. This function is shown in blue in figure 1(b). On the same figure, the orange line represents the $F(q)$, the total structure factor obtained after subtracting the Placzek (inelasticity) correction. Notice how the differential scattering cross section (orange line) oscillates around the Placzek function. When the inelasticity contribution is subtracted, the resulting function, the total structure factor $F(q)$, oscillates around zero, as shown in the figure. The total structure factor shows several peaks that are related to ordering on different real-space length scales. The analysis of this function is however complicated due to the presence of overlapping partial structure factors with composition-dependent weighting factors.

By performing the Fourier transform of $F(q)$ the total pair distribution functions (PDF) for the three samples were obtained and plotted as shown in figure 2(a). For visualisation purposes, the TNP5520 and TNP6510 $D(r)$ functions are shifted up. The dotted line at low r plotted for the three functions correspond to the density line around which the PDF should oscillate following $D(r\rightarrow 0) = -4\pi nr$.

The fitting of the pair distribution functions was done by approximating a Gaussian functions to each of the peaks. Each Gaussian has a standard deviation of $\sigma_{\alpha\beta}$ and it is centered around $r_{\alpha\beta}$, that corresponds to the bond distance between a pair of atoms α and β. The area below the Gaussian is proportional to the average coordination number $\overline{n}^{\beta}_{\alpha}$. Figure 2(b) shows the fitting of the peaks for the TNP4035 sample. The results of the fitting for the three samples is shown in table 2. These results are awaiting for the analysis of x-ray diffraction experiments for confirmation.

3 Spinel glass ceramic

Four glasses were measured using neutron diffraction. The samples were prepared at Corning Inc. by Aitken [1]. The composition of the four samples was: $(K_2O)_a$-$(ZnO)_b$-$(Al_2O_3)_c$-$(SiO_2)_d$-$(TiO_2)_e$ with $a = 0.0179, b = 0.1865, c = 0.1865, d = 0.5675, e = 0.0416$,. After quenching, four annealing stages were chosen to study the nucleation and crystalli-

Correlation	TNP4035			TNP5520			TNP6510		
$\alpha-\beta$	$\sigma_{\alpha\beta}$[Å]	$r_{\alpha\beta}$[Å]	$\overline{n}_{\alpha}^{O}$	$\sigma_{\alpha\beta}$[Å]	$r_{\alpha\beta}$[Å]	$\overline{n}_{\alpha}^{O}$	$\sigma_{\alpha\beta}$[Å]	$r_{\alpha\beta}$[Å]	$\overline{n}_{\alpha}^{O}$
P - O	0.050	1.52(3)	3.9*	0.043	1.52(3)	3.9*	0.044	1.52(4)	3.9*
Ti - O	0.062	1.93(3)	4.000(2)	0.075	1.89(9)	4.99(5)	0.095	1.96(3)	5.32(1)
Nb - O	0.118	1.96(7)	5.44(7)	0.109	1.940(2)	5.590(5)	0.066	2.005(6)	5.99(9)
O - O	0.097	2.50(6)	2.53(8)	0.084	2.500(1)	2.47(8)	0.077	2.49(8)	2.59(3)

Table 2: For each composition, the calculated average bond distance and coordination number with oxygen are shown with a typical measurement error. Fixed parameters are marked with an asterisk.

Sample	T [°C]	t [hour]	ρ[g/cm^3]	ρ_{pack} [g/cm^3]	n [atoms/cm^3]
Spinel_quenched			2.84(2)	1.443(2)	0.07440(1)
Spinel_750	750	4	2.860(4)	1.493(8)	0.0748(8)
Spinel_800	800	4	2.99(8)	2.1080(1)	0.0784(9)
Spinel_8001000	800 1000	4 2	2.97(1)	1.871(4)	0.0777(8)

Table 3: Characterization of the Spinel glass ceramic samples giving: the name, the annealing temperature and time, the density (ρ), the packing density (ρ_{pack}) of sample inside the vanadium can for the experiments and its number density (n).

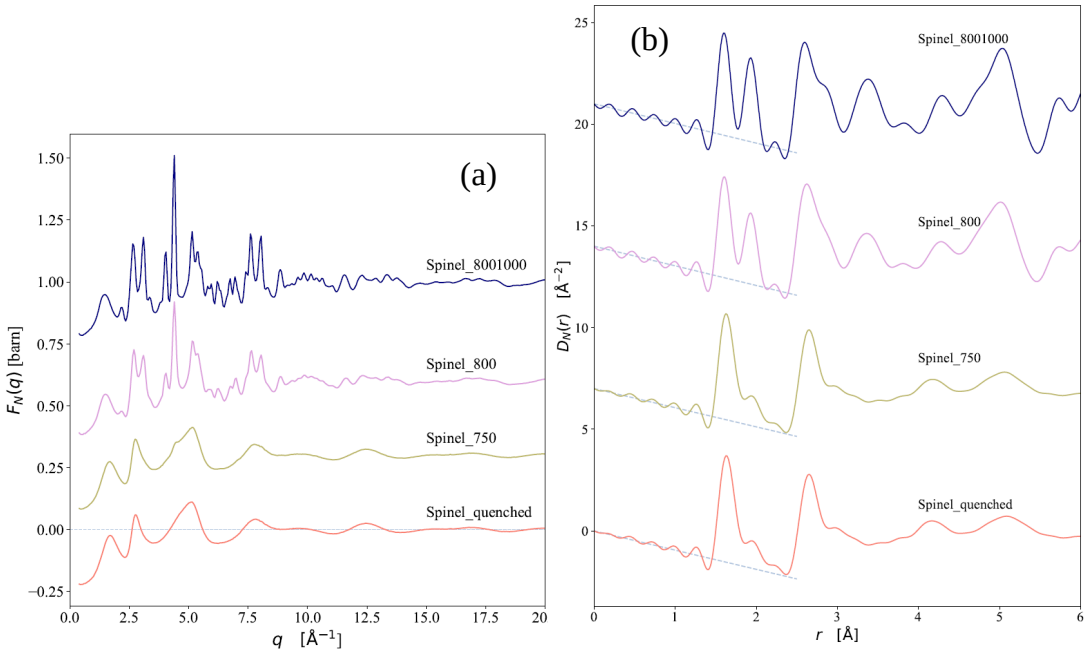

Figure 3: (a) F(q) for the Spinel glass ceramics. All the functions oscillate around zero but Spinel_750, Spinel_800 and Spinel_8001000 have been shifted up for clarity. (b)$D(r)$ for the Spinel glass ceramics. Notice how all the functions oscillate around the density line $-4\pi nr$ at low r. This is used as a consistency to check to verify the accuracy of the corrections performed.

sation processes. Table 1 shows the annealing stage for the four samples together with other the measured density and the packing density at the time of the experiments. The density measurements were performed by H. Mohammadi at the University of Bath using a He-gas pycnometer.

The analysis of data for the Spinel glasses was done following the same methodology as explained for the TNP system. The results obtained for this sample are shown in figures 3(a) and (b). The fitting of this sample is challenging due to the number of atoms that form the system. For this reason, no final results have been obtained yet for the coordination environment of this system. X-ray diffraction experiments are to be performed to complement the analysis and obtain the definite results.

References

[1] B. G. Aitken. High refractive index titanium-niobium phosphate glass. International patent number wo2018 / 140390 al. 2018.