Supplementary Materials

Unraveling the structural complexity of niobate units in aluminosilicate glasses and glass-ceramics

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Supplementary Materials S0

The base glasses' compositions in the ternary SiO_2–Na_2O–Al_2O_3 system have a fixed SiO_2 molar content (~66.6%) and two different Na_2O/Al_2O_3 molar ratios at 2.3 and 1. Therefore, one glass series has a composition in the peralkaline region ($Na_2O > Al_2O_3$) and the second one on the metaluminous joint ($Na_2O = Al_2O_3$). The glasses were made from dried pure oxide and carbonates mixed in stoichiometric proportions (SiO_2, Na_2CO_3, Al_2O_3, Honeywell Fluka). The mixtures were homogenized in an agate mortar and melted for 2 hours in a Pt-Rh crucible covered with a Pt-Rh lid at temperatures between 1500 and 1600 °C, depending on melt polymerization. The melt was rapidly quenched by removing the crucible from the furnace and immersing its bottom in water. The glasses obtained were then crushed and re-melted to ensure homogeneity. Portions of the base glass were finely ground, doped with commercially available $K_{0.5}Na_{0.5}NbO_3$ ceramic powder (KNN, d_{50} = 0.95 µm, CerPoTech, Norway) from 0.4 up to 20 mol%, then remelted in air with a dwell time of 1 h at 1500 °C and 1650 °C, respectively for the NA66.10 and the NA66.17 series. Detailed compositions are available in Table S0.

Table S0: Composition of the two glass systems, as determined by ICP analysis (recalculated as mol%) and thermal events; data are from Cicconi et al. 2023, doi.org/10.1016/j.omx.2023.100228

sample	SiO2	Al2O3	Na2O	K2O	Nb2O5	*Tg* (°C) ±2	*Tx* (°C) ±5
NA66.10	66.3	10.4	23.3	0.0	-	542	922
_0.4KNN	66.4	10.0	23.3	0.1	0.2	542	945
_0.8KNN	66.2	9.9	23.3	0.2	0.4	548.7	965
_1.5KNN	65.7	9.9	23.4	0.4	0.8	555	922
_2.9KNN	64.7	9.7	23.4	0.7	1.5	571	932
_5.4KNN	63.1	9.5	23.4	1.4	2.7	589	938
_10KNN	60.4	9.3	23.1	2.5	4.7	598	924
_20KNN	53.4	8.0	23.7	5.0	10.0	611	812
NA66.17	66.3	16.7	17.0	0.0	-	792**(5)**	1354
_0.4KNN	66.4	16.6	16.7	0.1	0.2		
_0.8KNN	66.2	16.5	16.7	0.2	0.4		
_1.5KNN	65.7	16.4	16.8	0.4	0.8	748	1226
_2.9KNN	64.6	16.1	16.9	0.7	1.7	731	1192
_5.4KNN	63.0	15.7	17.1	1.3	2.9	708	1064
_10KNN	60.8	14.7	17.1	2.5	4.8	679	901
_20KNN* (xx17.20)	51.2	12.8	17.6	4.8	13.6		

*** crystallised during quench. Label used: xx17.20**

Table S0.2: Synthesis conditions of the two glass ceramic samples and the resulting crystallized phase.

sample	T crystallization (°C)	Holding time (h)	Phase/ Space group	
GC10-10	900	2	$K_xNa_{(1-x)}NbO_3$	*Pbcm (Pbma)*
GC10-17	900	4	$K_xNa_{(1-x)}NbO_3$	*Pbcm* (*Pbma*)

Supplementary Materials S1

The analysis and the results of the KNN reference crystalline material are presented. The structure factor S(Q) and the experimental PDF, G(r) obtained by Fourier transformation of the reduced structure factor are shown in Figure S1. The G(r) represents the distribution of interatomic distance and has been refined via PDFgui [1]. The calculated structure shows a good agreement with the experimental one, and the refined parameters are:

label	Space group	*a, b, c* (Å)	*V* (Å^3)
KNN	*Amm2*	3.93677/ 5.67191/ 5.64214	125.98

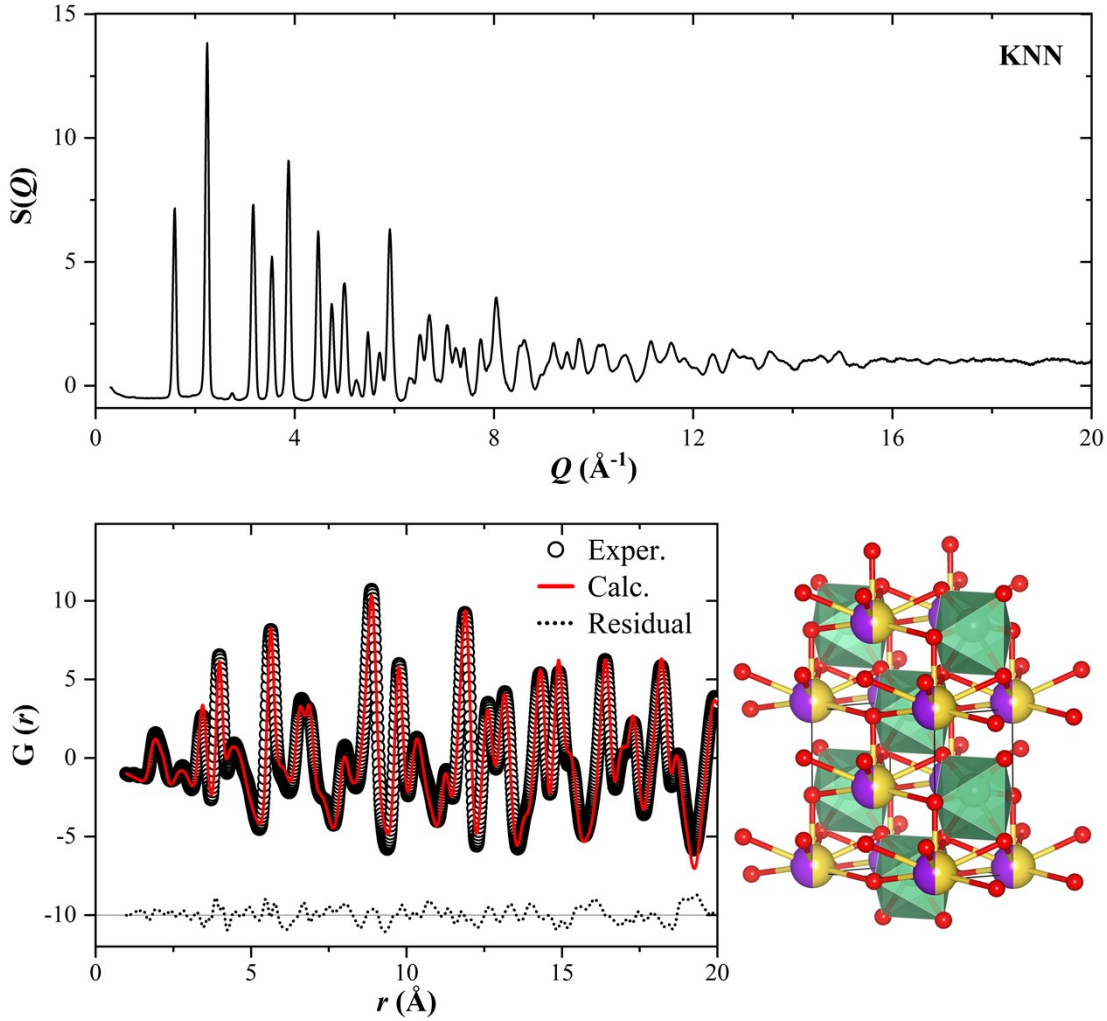


Figure S1: The structure factor S(*Q*) of the KNN reference crystalline material. The experimental G(*r*) obtained by Fourier transforming the reduced structure factor has been refined via PDFgui, and the calculated signal and the residual are shown.

The average bond lengths and correlations from the refined structure shown in Figure S1 are listed in Table S1. The Nb–O bond distance is an average from long and short bonds, peaking around 1.90 and 2.14 Å as clearly visible from the split of the experimental PDF (Figure 2, main text).

Table S1: Average bond lengths and correlations from the KNN refined structure via PDFgui.

Correlation	Average distances	Polyhedra Distortion index*
Nb – O	2.0036 Å	0.05891
A – O	2.8308 Å	0.07283
A – Nb	3.40 Å	-
Nb – Nb	4.00 Å	-

* Baur's polyhedra distortion index calculated by Vesta®. [2,3]

For comparison, the bond distances obtained from the deconvolution with mathematical functions (Gaussians) of the real-space data for the crystalline material KNN and the NA66.10-04 glass (see Figure 2 in the manuscript) are reported below in Table S1.2.

Table S1.2: Bond distances (center of the Gaussian functions) from the signal decomposition of the real-space data for the crystalline KNN and the NA66.10-04 glass (see Figure 2 in the manuscript)

Correlation	**Crystalline KNN**
Nb – O	1.89(2) Å
Nb – O	2.11(6) Å
A – O	2.7(6) Å
A – O	2.9(9) Å
A – Nb	3.43(1) Å
Nb – Nb	3.99(1) Å
	Glass NA66.10-0.4KNN
T – O	1.65(1) Å
A – O	2.28(9) Å
O – O	2.63(8) Å
T – T	3.14(1) Å

Supplementary Materials S2

Figure S2 shows the experimental pair distribution function $G(r)$ obtained from Fourier transformation of the total scattering structure factor $S(Q)$ for the two glass series having increasing KNN contents: a) NA66.10 series; b) NA66.17 series.

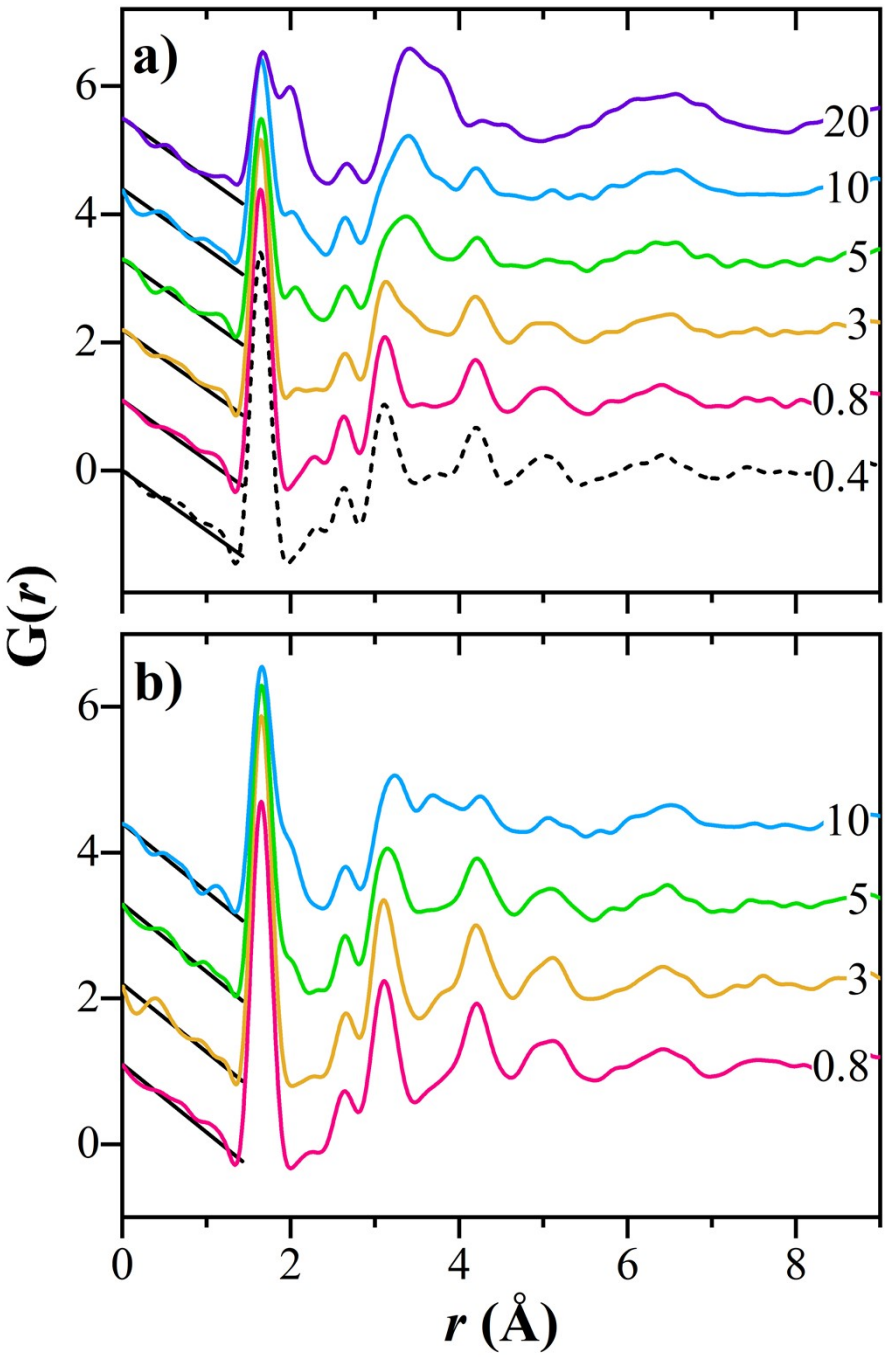


Figure S2: The experimental pair distribution function $G(r)$ obtained from Fourier transformation of the total scattering structure factor for the two aluminosilicate glass series having increasing KNN contents (from 0.4 mol% to 20 mol%). a) NA66.10 series; b) NA66.17 series.

Supplementary Materials S3

NMR data of the two glass series.

The ^{27}Al MAS NMR spectra of selected specimens were successfully simulated using a single component according to the Czjzek distribution model of quadrupolar parameters[4] (see Figure S3). No significant amounts of higher coordinated Al species can be detected, and crystallization has no apparent effect on the NMR spectra. The ^{93}Nb MAS NMR spectra for the two glass series and the GCs samples are shown on the right panels of Figure S3. The ^{93}Nb linewidth of the NA66.10 glasses stays nearly invariant as a function of KNN content, while strong variations exist in the metaluminous series NA66.17.

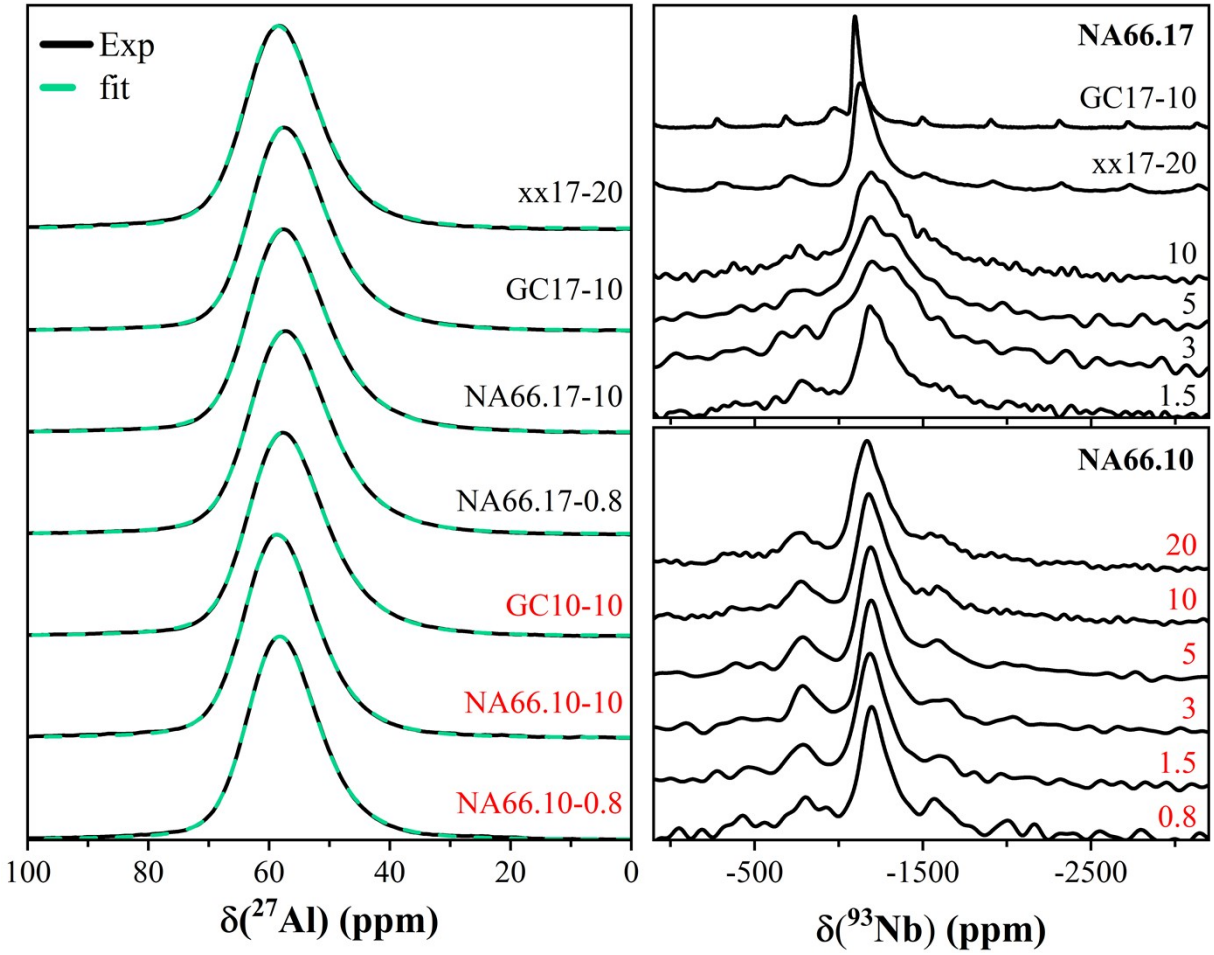


Figure S3 Left panel: ^{27}Al MAS NMR spectra for selected samples in the two glass series. The dashed lines represent the simulated spectra according to the Czjzek distribution model of quadrupolar parameters. Right panels: The ^{93}Nb MAS NMR spectra for the glasses in the NA66.10 series barely change, while strong variations are observed in the NA66.17 series.

Supplementary Materials S4

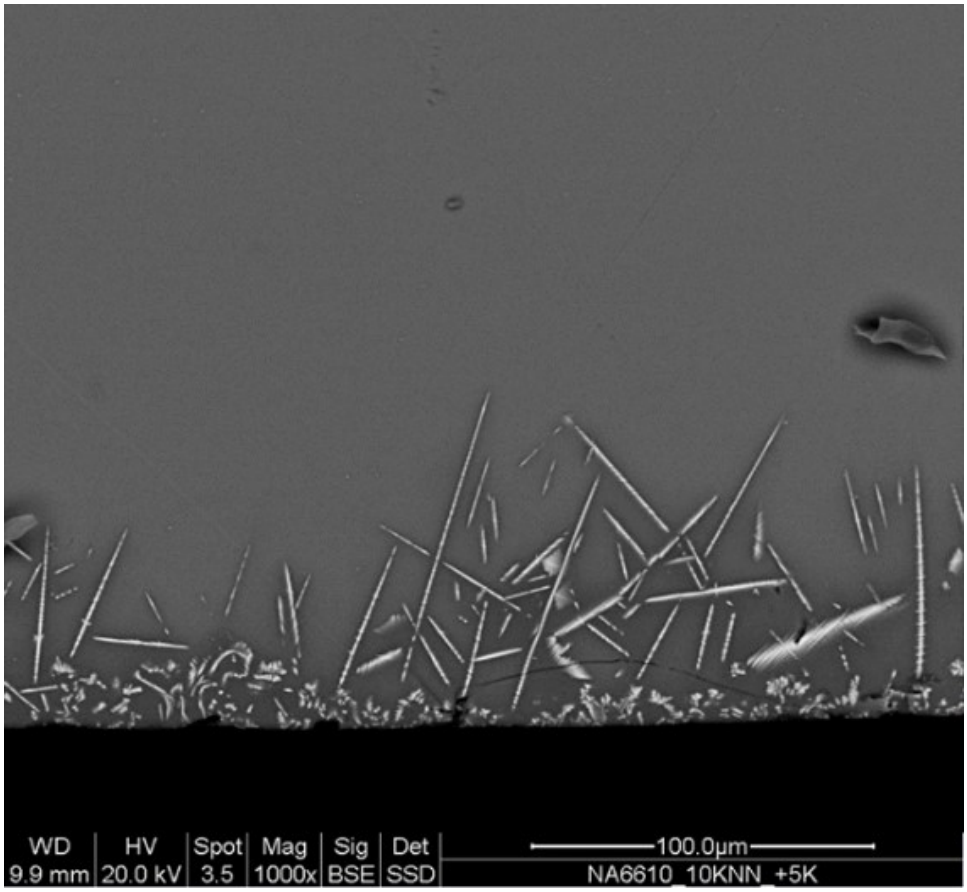
Table S2: Results from the pair-function method

The pair-function method was developed by Mozzi and Warren [5,6] to analyse amorphous SiO_2 and B_2O_3 to obtain the average distances and coordination numbers. This method was used here to estimate the interatomic distances and the cation–oxygen coordination of the niobo-aluminosilicate glasses and GCs. The procedure used is described in details in [7].

	Si–O		**Al–O**		**Nb–O**		**Na–O**		**O–O**		**K–O**	
	r_{Si-O} (Å)	N_{Si-O}	r_{Al-O} (Å)	N_{Al-O}	r_{Nb-O} (Å)	N_{Nb-O}	r_{Na-O} (Å)	N_{Na-O}	r_{O-O} (Å)	N_{O-O}	r_{K-O} (Å)	N_{K-O}
NA66.10 series												
0.4 KNN	1.63	4	1.74	4	-	-	2.34	4.1	2.66	5.5	2.7	5.2
0.8 KNN	1.63	4	1.74	4	-	-	2.33	4.1	2.66	5.5	2.7	5.2
3 KNN	1.63	4	1.74	4	2	6.1	2.34	4.1	2.66	5.5	2.7	5.2
5 KNN	1.63	4	1.74	4	2	6	2.3	4.3	2.66	5.5	2.7	5.2
10 KNN	1.63	4	1.74	4	2	5.9	2.34	4.2	2.66	5.5	2.7	5.2
20 KNN	1.63	4	1.74	4	1.99	5.9	2.34	4.2	2.66	5.5	2.7	5.2
NA66.17 series												
0.8 KNN	1.63	4	1.74	4	-	-	2.32	4	2.66	5.5	2.7	5.2
3 KNN	1.63	4	1.73	4	1.86 2.17	4.1 0.4	2.36	4.0	2.68	5.5	2.7	5.2
5 KNN	1.63	4	1.73	4	1.96	5.8	2.36	4.1	2.67	5.5	2.7	5.2
10 KNN	1.63	4	1.74	4	1.98	5.9	2.35	4.2	2.67	5.5	2.7	5.2
Glass-ceramics												
GC66.10-10	1.63	4	1.75	4	2	6.1	2.34	4.4	2.66	5.5	2.7	5.2
GC66.17-10	1.63	3.9	1.76	4	1.94 2.21	5.2 0.7	2.36	4	2.67	5.5	2.7	5.2

Supplementary Materials S5

SEM images in Electron Backscattering are very sensitive to the chemical composition and any Nb-rich region is brighter. As the melting point of KNN ceramics around 1150 °C is well below the temperatures used for the synthesis, if the solubility limit of Nb had been reached, residual Nb-rich liquid droplets should be noticeable. The total absence of such droplets and the homogeneous Nb concentration measured by EDX support a total solubility of Nb in the glass.



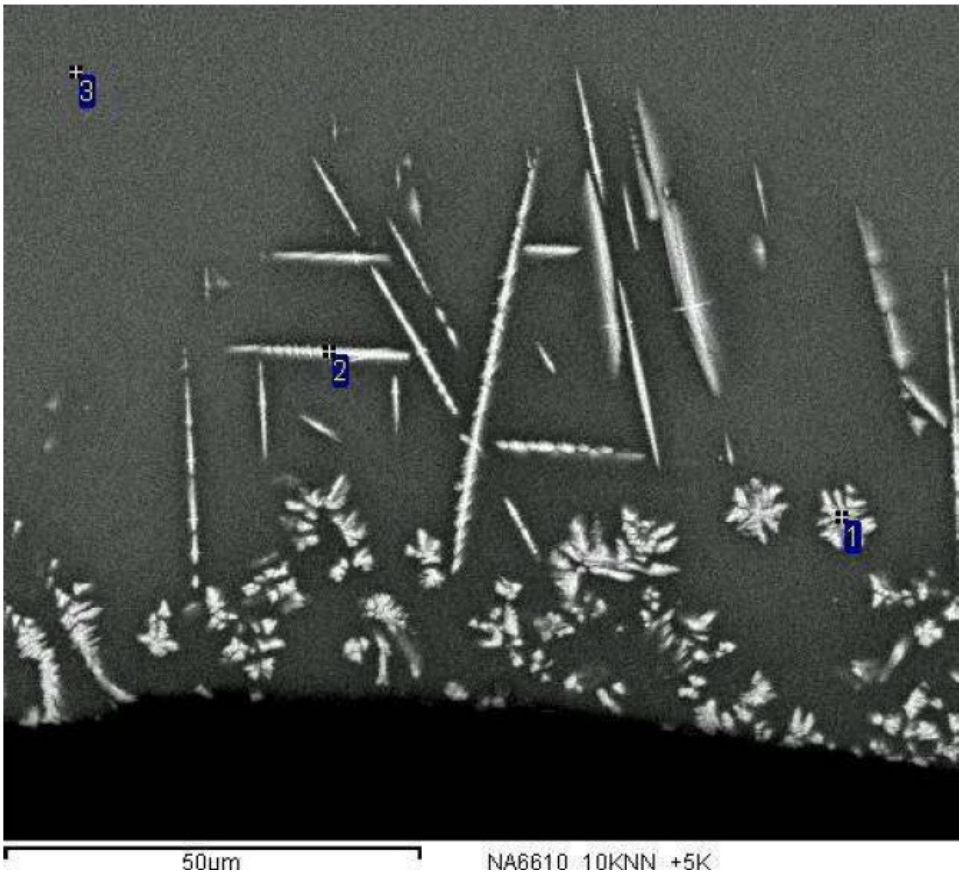


Figure S5: SEM image and EDX point analysis of the surface crystallization (bright spots - points 1 and 2) of a glass-ceramic obtained from the NA6610_10KNN sample and of the glass matrix (point 3).
The atomic% from the EDX are reported in the table below:

EDX Spectrum	O	Na	Al	Si	K	Nb
1	68.06	11.08	3.2	7.76	1.85	8.05
2	67.04	12.62	3.02	8.56	2.03	6.74
3	65.73	8.23	4.81	15.58	3.09	2.56

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