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Atomic-Level Insights into Niobium-Modified Borophosphate Glasses

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Abstract

This paper reports the use of molecular dynamics simulations to obtain structural information on sodium borophosphate glasses containing niobium. The results were compared with high-energy X-ray diffraction, neutron diffraction, Raman and IR spectroscopy, X-ray absorption measurements, and NMR data to investigate the effects of niobium incorporation on the structure and properties of these glasses. The simulation results show good agreement with the experimental data. As expected, both boron (B) and phosphorus (P) act as tetrahedral network formers. The number of Nb-Nb linkages increases with increasing niobium content, initially leading to corner-sharing and then forming interconnected NbO₆ units. At low niobium content, Nb adopts an off-center position within the octahedral site, and the distortion of the NbO₆ units increases as niobium content rises. Additionally, as the niobium concentration increases, more phosphorus atoms form bonds with other network formers.

Keywords: Oxide glasses, Molecular dynamics simulation, Glass structure.

1. Introduction

Phosphate glasses have attracted significant interest in both scientific research and industrial applications due to their unique structural and chemical properties [1-9]. However, the incorporation of boron atoms into phosphate glasses has been found to increase the glass transition temperature, improve the conductivity, enhance mechanical hardness, improve chemical durability and stability, and enhance the quality of transparency and refractive index of the glass [10-11]. Borophosphate glasses, a subclass of phosphate glasses, have gained considerable attention in recent years due to their unique structural characteristics and versatile properties. These glasses, composed of a network of boron oxide (B₂O₃) and phosphorus pentoxide (P₂O₅).

Much effort has also been given recently to the glasses from which non-linear optical (NLO) effects originate, due to their potential for optoelectronic applications, such as electro-optic switches and modulators. In principle, the nonlinear optical properties of materials under an electromagnetic field result from the generation of a polarisation. This polarisation can be expressed in terms of the linear susceptibility χ which accounts for the linear optical index [12]. A recent study of this effect has shown that large values of NLO susceptibility $\chi^{(3)}$ are observed in glasses containing an empty *d* shell transition metal ions such as Nb^{5+} [13]. NLO effects in these glasses have motivated the study of the local atomic environment of Nb^{5+} [12, 14]. One of the such studies reported by Wetherall et al [15] is focused on sodium borophosphate glasses containing niobium. Molecular dynamics simulation can provide further information on the structure of these complex glasses, extended structural details, and provide a three-dimensional visualisation of the structure.

Sodium borophosphate glasses containing niobium have been studied by Wetherall et al [15] using diffraction, X-ray absorption spectroscopy and NMR studies. Previous spectroscopic studies of these glasses have shown that the addition of small amounts of Nb_2O_5 results in isolated NbO_6 octahedra [15, 12]. However, when the concentration of Nb_2O_5 is increased there begins to be corner sharing of octahedra and finally a three-dimensional network of corner sharing NbO_6 and they take the role of a network former at higher concentration [12]. The structure of these glasses is complicated as it is a multi-component composition and contains more than one network former.

Although Zachariasen's model [16] and several rules concerning vitreous structures of borates [17, 18] have been published, there are several hypotheses to describe the complexity of boron-oxygen bonding. Experimentally, it is widely accepted that borons have threefold coordination [19], however, a fourfold-coordinated tetrahedron (BO_4) is also found in binary alkaline borate glasses [20-22]. On the other hand, the crystal structure of most Nb_2O_5 phases is mainly composed of octahedra with niobium atoms in the centre, surrounded by six oxygen atoms. There are different Nb_2O_5 phases which are strongly dependent on the method of preparation and annealing conditions [23]. The investigations into the crystal structure of the Nb_2O_5 polymorphs which were reported in the literature showed a great variety of polymorphs with different arrangements [24, 25].

Although Wetherall et al [15] have drawn a successful interpretative picture of the complex structure of borophosphate glasses containing niobium based on several experimental results, it still deserves further investigation using computer modelling. This in turn can provide more information about the medium range order and can present comparable models to the experimental results.

2. Inter-atomic Potentials

Three compositions of sodium borophosphate glasses containing niobium were simulated using version 2.18 of the DLPOLY code [26]., as detailed in Table 1. Interactions between P–O, O–O, Na–O, B–O, and Nb–O were described using Buckingham rigid ion potentials with a Coulomb component, as shown in Equation 1. The potential parameters were sourced from Teter's [27], work and are listed in Table 2.

$$V_{ij}(r) = \frac{q_i q_j}{4\pi\epsilon r} + A_{ij} \exp\left(\frac{-r}{\rho_{ij}}\right) - \frac{C_{ij}}{r^6} \quad \text{Equation 1}$$

Table 1: Details of models compositions.

Sample	Nb ₂ O ₅ (mol%)	Na ₂ B ₄ O ₇ (mol%)	NaPO ₃ (mol%)	Density gcm ⁻³	No of atoms	Box length (Å)
Nb11	11.0	4.5	84.0	2.81	1111	24.47
Nb22	22.0	4.5	73.5	2.92	1146	25.15
Nb36.5	36.5	3.0	60.0	3.48	1189	25.03

Table 2: Pair Potential Parameters for two-body interactions for the Glass Matrix

<i>i-j</i>	q _i (e)	A _{ij} (eV)	ρ _{ij} (Å)	C _{ij} (eV Å ⁻⁶)
P-O	3.0	27722	0.1819	86.86
O-O	-1.2	2028	0.3436	192.58
Na-O	0.6	4383	0.2438	30.70
Nb-O	3.0	11448	0.2280	95.19
B-O	1.8	5312	0.1910	20.70

3. Computational Details

Running DL_POLY_2 simulations requires three essential input files: CONTROL, CONFIG, and FIELD. The CONTROL file specifies all control variables necessary for the simulation, including the type of molecular dynamics (MD) run, the data collection parameters, and the total run time. The CONFIG file contains the initial atomic configuration. At the beginning of the simulation, atomic positions are randomly assigned to ensure an unbiased distribution of atom types, avoiding any initial structural correlations. This file also defines the unit cell dimensions, system density, and atomic labels. The FIELD file provides the force field definitions that describe the interatomic interactions. Once these inputs are prepared, the simulation is executed. Atoms interact over time within a periodic boundary condition (PBC), meaning the simulation cell is replicated along all directions to mimic an infinite system. The atoms are effectively confined within a primitive cell, surrounded by an infinite array of identical cells, creating a periodic lattice.

To ensure numerical stability and accurate energy conservation, the MD simulation uses a time step of 1 femtosecond (fs, 10^{-15} s). A Berendsen NVT thermostat [28] with a relaxation time of 2 picoseconds (ps) is applied to regulate the temperature and achieve final densities consistent with experimental values. A short-range cut-off of 10 Å is used for non-Coulombic pairwise interactions. The Coulombic interactions are calculated using the Ewald summation method [29, 30], with a real-space cut-off of 11.8 Å and a precision of 10^{-5} . Initially, the system is heated to a high temperature (e.g., 6000 K for 40,000-time steps) to randomize atomic positions fully and eliminate any memory of initial structure. The temperature is then gradually reduced to just above the glass melting point. The simulation consists of six stages, summarized in Table 3. Equilibration stages at 6000 K, 3000 K, and T_m (where T_m is ~ 300 K above the melting temperature of the glass). These stages apply linear thermal expansion coefficients of 1.03, 1.015, and 1.005, respectively. A temperature quench from T_m to 300 K, spanning $(T_m - 300) \times 50$ time steps, corresponding to a quench rate of 10^{13} K·s $^{-1}$, a typical value in MD simulations of glasses [31, 32], though much faster than experimental rates due to computational limitations. During these four stages, atomic velocities are rescaled every five-time steps. Finally, two isothermal baths at 300 K are run, each for 40,000 time steps one with and one without equilibration. Structural parameters are extracted during the final stage, sampled (every 200 time-steps) to include disorder due to thermal vibrations, which is present in the experimental results.

Table 3: The MD stages for melt-quenched glass.

stages	Program	Temp (K)	Time steps	Process	Thermal Expansion Coefficient (%)
1	Bath	6000	40000	Equilibrate	103.0
2	Bath	3000	40000	Equilibrate	101.5
3	Bath	$T_m > T_{melting}$	40000	Equilibrate	100.5
4	Quench	$T_m - 300$	$(T_m - 300) * 50$	Quench	100.5
5	Bath	300	40000	Equilibrate	100.0
6	Bath	300	40000	Collect	100.0

A successful run of DL_POLY_2 generates five output data files at the end of each stage, OUTPUT, REVCON, STATE files (Ascii file), HISTORY and REVIVE files (binary file). Additionally, an extra readable file is created at the end of stage 6 called RDFDAT. The OUTPUT file is a total summary of the job run such as starting and final configurations, instantaneous and rolling-averaged thermodynamic data, job timing data, and radial distribution functions are available in the OUTPUT file from stage 6. The REVCON file contains the restart configuration of the atoms at the end of each stage so it is basically the CONFIG file after running the simulation. REVIVE and STATE files contain the data for a number of thermodynamic quantities [28]. The HISTORY file records a time ordered sequence of the atomic coordinates, velocities and forces at the specified time steps to facilitate the analysis of the results. Finally, the radial distribution functions are stored within the RDFDAT file as well. Analysing the data requires the OUTPUT, HISTORY and REVCON files from stage six only. The radial distribution function, the coordination numbers and the bond angle distributions were obtained using programs called “xanal” and “xhst-hsc” developed by Du Jincheng from Alfred State University [33]. Table 4 summarises the analysis of the resulting files from stage six and the programs used to analyse them with their output files of structural information. However, the “0analysis” file which is essential in each run must be modified for each analysis stage to meet the requirements.

Table 4: The input and output files for analysing MD data.

The required files	Running program	Output file	Containing Information
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OUTPUT + HISTORY + 0analysis file	xanal_O2	md.tdfcn	The radial distribution function and the average coordination number
	xanal_O2	md.bad	Bond angle distributions
	xhst_hsc-gm2	md.hscstd	The distribution of coordination number and Q^n distribution
REVCON	DLPXYZ	XYZ.xyz	The image of the model

4. Results

4.1 The image of the models

The images of Nb22 and Nb36.5 glass models are shown in Figure 1 using Vesta Software. The pink tetrahedra depict PO_4 units, the orange polyhedra represent BO_n groups, the large spheres correspond to Na atoms, and the green polyhedra illustrate NbO_n units.

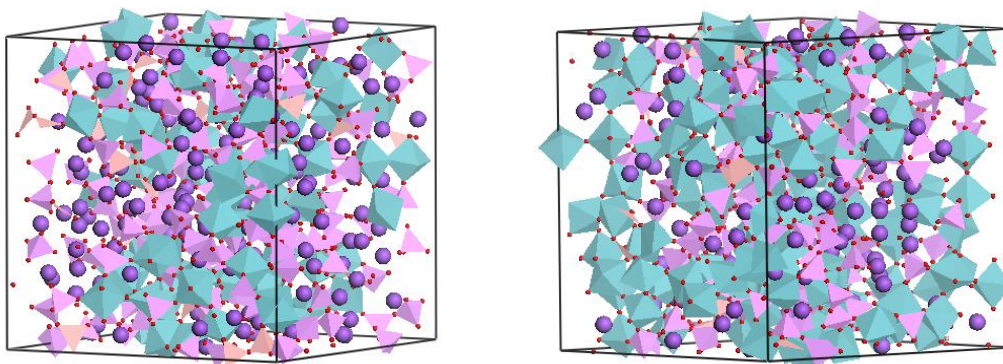


Figure 1: The Nb22 model image is to the left and the Nb36.5 image is to the right.

4.2 Distribution functions and coordination numbers

Figures 2 and 3 show the partial correlation functions $T_{ij}(r)$ for the models, and the sequence of interatomic correlations are listed in Table 5 in comparison with the experimental values [15]. The first interatomic correlation found in the range of 1.41-1.46 Å is due to B–O correlation which becomes shorter upon the addition of Nb. It has been reported that boron with fourfold coordinated has a bond length of 1.48 Å whilst three-coordinated boron has a bond length of 1.37 Å [15]. According to the models the B–O coordination has an average value of 3.28-3.50. The P–O mean distance is well known at ~1.51 Å with a coordination number of 4. The third parameter listed in Table 4 is the Nb–O correlation. Based on EXAFS results [15], the Nb–O correlation has a large

spread in bond distance, ranging from 1.75 to 2.05 Å. In the experimental results, there are two contributions to Nb-O bond distances as listed in Table 5. The presented models gave an average Nb-O bond distance of around 1.96 Å, with a coordination number of ~ 6 in all models.

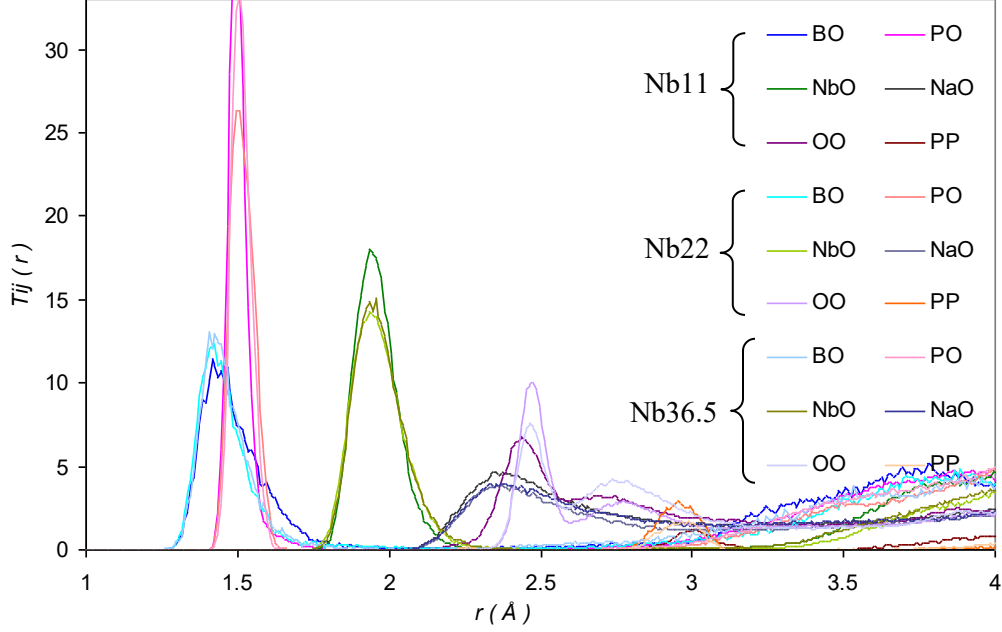


Figure 2: Partial correlation functions for Nb11, Nb22 and Nb36.5 models.

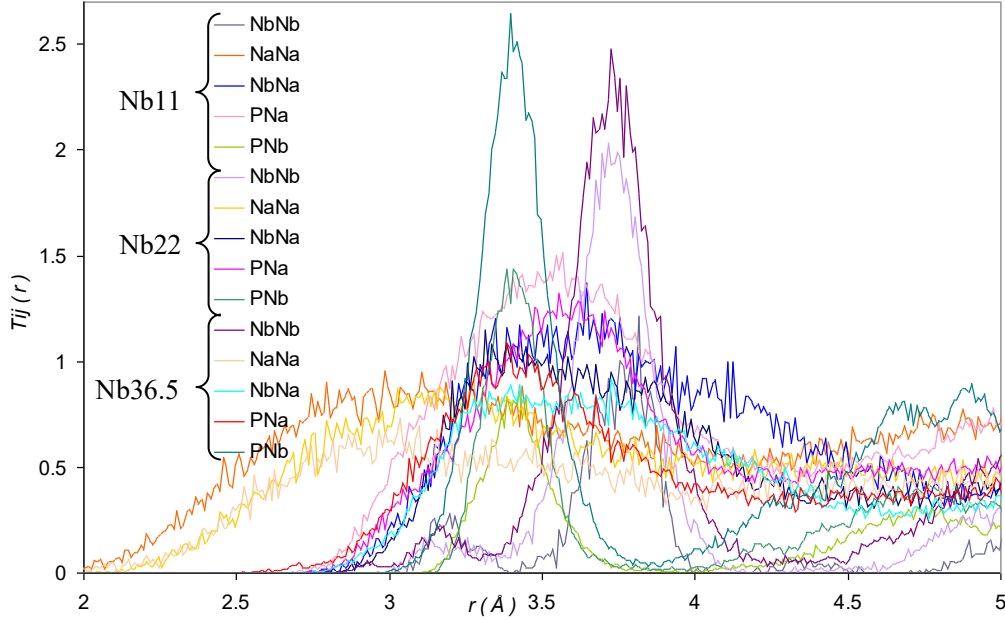


Figure 3: Partial correlation functions for the three models.

Table 5: Details of the bond distances and the coordination numbers of the models.

Sample	Correlation	Distance (Å)		Coordination number		Cut-off distance (Å)
		EXPT ± 0.02	Model ± 0.02	EXPT $\pm 15\%$	Model ± 0.3	Model
Nb11	B–O	-	1.46	-	3.50	2.55
	P–O	-	1.51	-	4.00	2.53
	P–O _{nb}	-	1.49	-	2.45	2.00
	P–O _b	-	1.55	-	1.55	2.00
	Nb–O	-	1.98	-	5.87	2.68
	Na–O	-	2.41	-	4.79	2.90
	O–(B/P)–O	-	2.48	-	3.35	2.58
Nb22	B–O	1.46	1.43	3.9	3.28	2.55
	P–O	1.54	1.51	3.9	4.00	2.53
	P–O _{nb}	-	1.50	-	2.53	2.00
	P–O _b	-	1.53	-	1.53	2.00
	Nb–O	1.75	-	0.9	-	-
	Nb–O	2.03	1.96	4.9	5.75	2.68
	Na–O	2.37	2.41	3.4	4.57	2.90
Nb36.5	O–(B/P)–O	2.50	2.48	3.0	2.89	2.58
	B–O	1.42	1.41	4.0	3.32	2.55
	P–O	1.53	1.51	3.9	4.00	2.53
	P–O _{nb}	-	1.50	-	3.1	2.00
	P–O _b	-	1.55	-	0.9	2.00
	Nb–O	1.79	-	0.9	-	-
	Nb–O	2.02	1.94	4.9	5.79	2.68
	Na–O	2.37	2.42	3.3	4.95	2.90
	O–(B/P)–O	2.51	2.47	3.0	2.40	2.58

From the model it can be concluded that Na is coordinated to a total of approximately 5 oxygen atoms which is higher than the value reported by Wetherall et al [15] of about 3.4. The O–O bond length is typically found in the region of 2.47-2.52 Å. This shell originates from the O–(P)–O and the O–(B)–O distance where the oxygen atoms are coordinated to an average of three other oxygen atoms.

Table 6 details the network former connections in the three models. As expected and widely reported the P–P correlation is found in the region from 2.9-3 Å with P–P connectivity decreasing

with increasing Nb oxide content. The B-B distances were determined to be in the range of 2.78-2.84 Å, and the coordination number is much less than one. While the number of phosphorus atoms surrounding B decreases with increasing Nb content, the coordination of boron with Nb increases.

Fair agreement was obtained by comparing the models results in Table 6 with the NMR results from Wetherall et al [15]. The notation of $P^m_{(n)}$ was used to explain the experimental results by Wetherall et al [15], where m is the number of bridging oxygen atoms and n is the number of links to network formers other than P, as given in Table 5. From the NMR results, it was concluded that at low Nb content there are 0-1 P-P linkages, which is slightly less than the average coordination number of 1.53 for P-P linkages, obtained from the Nb11 model. Additionally, P-X coordination is in the range of 1-2 based on NMR results where P-X represents P-B plus P-Nb. According to Nb11 model this summation is equal to 1.03, which is in good agreement with NMR results. This suggests that Nb could be a "conditional" network former. The agreement is good as well when making a similar comparison of B-B linkage of 0 from NMR and 0.80 from the model. However, although B-X coordination of 3-4 is obtained from NMR, B-P plus B-Nb from the model is $1.29+1.08=2.37$ which is less. This can be attributed to the cut-off distances used to measure the B-P plus B-Nb coordination numbers.

From Figure 3 the Na-Na peaks are very broad and cover a range of 2.88- 3.23 Å. The model concluded that the coordination numbers of Na with both B and Nb is low and decreases with increasing Nb content. On the other hand, Na is highly coordinated to phosphate at low Nb content while it tends to decrease at high Nb content as some Na is coordinated to Nb instead. The Nb-Nb correlation is sharp at about 3.78 Å and the sequence of the peaks indicates that the Nb-Nb coordination number increases with the addition of Nb₂O₅ content. Table 7 reports the predicted cation-cation coordination numbers from Wetherall et al [15] in comparison to those values obtained from the Nb11 model. Generally speaking, the network linkages from P are primarily to P and Nb, and less to B. The network linkages from B are primarily to P, some to Nb and less to B. The network linkages from Nb (acting as a conditional network former) are primarily to P, with some to Nb. The network modifier Na is primarily compensating non-bridging oxygen's on P.

Table 6 : Details of network former connections in the three models

Sample network former	Correlation	distance (Å)	Coordination number	Cut-off distance (Å)
		Model	Model	Model
Nb11				
P	P-P	2.99	1.53	3.53
	P-B	2.97	0.28	3.61
	P-Nb	3.45	0.75	4.00
B	B-B	2.81	0.80	3.51
	B-P	2.94	1.29	3.58
	B-Nb	3.28	1.08	3.66
Nb22				
P	P-P	2.96	1.46	3.53
	P-B	2.96	0.27	3.61
	P-Nb	3.42	1.17	4.00
B	B-B	2.78	0.35	3.51
	B-P	2.96	1.07	3.58
	B-Nb	3.28	1.64	4.00
Nb36.5				
P	P-P	2.99	0.89	3.53
	P-B	2.96	0.79	3.61
	P-Nb	3.42	2.38	4.00
B	B-B	2.84	0.00	3.51
	B-P	2.95	0.78	3.58
	B-Nb	3.20	2.51	4.00
Experimental results from ³¹ P and ¹¹ B NMR				
Nb11				
$P_{(1)}^2$	P-P		0-1	
$P_{(2)}^2$	P-X		1-2	
$B_{(2)}^2$	B-B		0	
	B-X		3-4	

Table 7: Comparison of the schematic structure from Wetherall et al [15] with the results from Nb11 model. (Where “ ? “ means no prediction was made).

Correlation	Coordination number predicted from schematic	distance (Å)	Coordination number	Cut-off distance (Å)
		Model	Model	Model

P-P	0.33	2.99	1.53	3.53
P-B	0.67	2.97	0.28	3.61
P-Nb	1.11	3.45	0.75	4.00
P-Na	3.00	3.61	5.06	4.50
B-B	0	2.81	0.80	3.51
B-P	3	2.94	1.29	3.58
B-Nb	1	3.28	1.07	3.66
B-Na	?	3.17	3.33	3.92
Nb-Nb	1	3.78	1.09	4.17
Nb-P	5	3.45	3.13	3.40
Nb-B	0	3.28	0.91	3.90
Nb-Na	?	3.48	4.09	4.25
Na-P	4	3.60	4.03	4.22
Na-B	0	3.16	0.62	3.85
Na-Nb	0	3.64	0.89	4.15
Na-Na	?	2.89	2.95	3.66

4.3 Bond angle distribution and the connectivity

The connectivity between the PO₄ tetrahedra is represented by the P-O-P bond angle distribution and it obviously decreases with the addition of more Nb oxide content. The O-P-O bond angle confirms the tetrahedral P environment with an angle of 109.8°, as illustrated in Figure 4. Table 8 shows that increasing Nb content causes further depolymerisation of the phosphate network as expected.

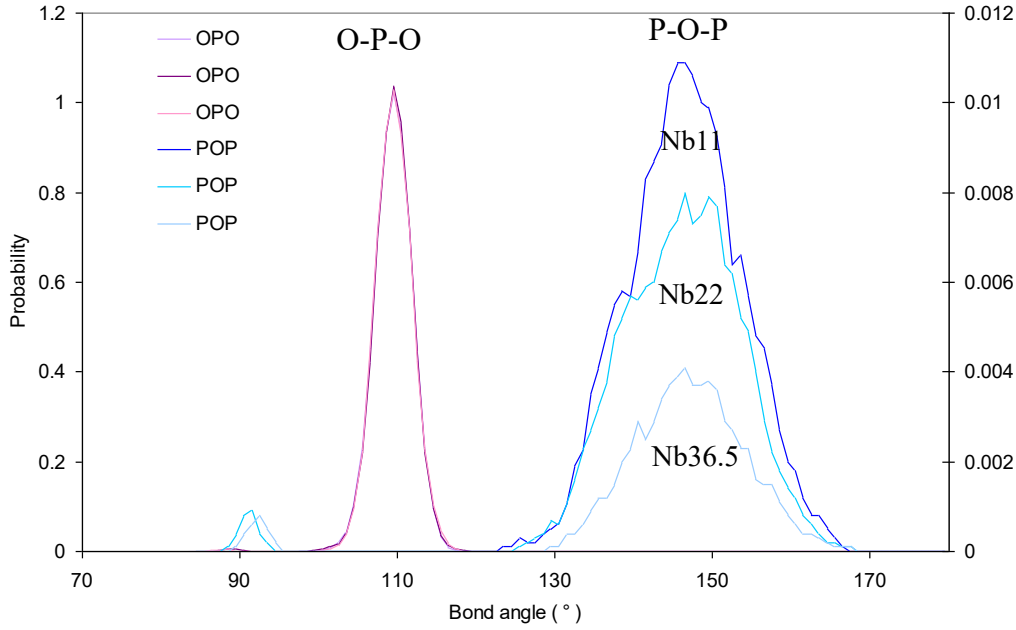


Figure 4: Bond angle distributions of the models.

Table 8: Details of Q^n distribution obtained from the three models.

Q^n relative amount %	Nb11	Nb22	Nb36.5
Q^0	11	14	31
Q^1	35	40	49
Q^2	43	35	19
Q^3	11	11	1
Average n	1.54	1.43	1

4.4 Comparison with diffraction studies

A great deal of interest in modelling any structure is its characteristic interference function $i(Q)$. The $i(Q)$ data for the three models in comparison with the experiment are shown in Figure 5, and their corresponding $T(r)$ are shown in Figure 6. The maximum Q values used in the Fourier transform of the X-ray and neutron $i(Q)$ using Lorch function are listed in Table 9. All experimental $T(r)$ functions follow a similar profile with three major features at around $1.52\text{\AA}$,

2Å, and 2.5Å corresponding to the P-O, Nb-O, and O-O nearest distances, respectively. The B-O correlation is included on the lower side of the P-O peak. A continuous decrease in the intensity of the O-O peak and a continuous increase in the Nb-O intensity peak with increasing Nb₂O₅ content were observed in both the models and experimental results. Although, there were no XRD or ND data for the Nb11 sample, the model was assumed to be as reasonable as the other models. The sensitivity of X-ray diffraction to the niobium–oxygen correlation is observable in $XRD\ T(r)$ while neutron diffraction highlights the phosphorus–oxygen and oxygen–oxygen correlations. There are differences in relation to the amplitude observed in $T(r)$ at low r and even more at high r . Nevertheless, based on the difficulties modelling such multi-component systems the $i(Q)$ presented by the models have the similar features and trends as those obtained experimentally.

Table 9: Details of Q_{max} (Å⁻¹) used in Fourier Transform of the $XRD\ i(Q)$ and $ND\ i(Q)$ using Lorch function.

The sample	Nb11	Nb22	Nb36.5
$XRD\ Q_{max}$	18	16	15
$ND\ Q_{max}$	35	35	35

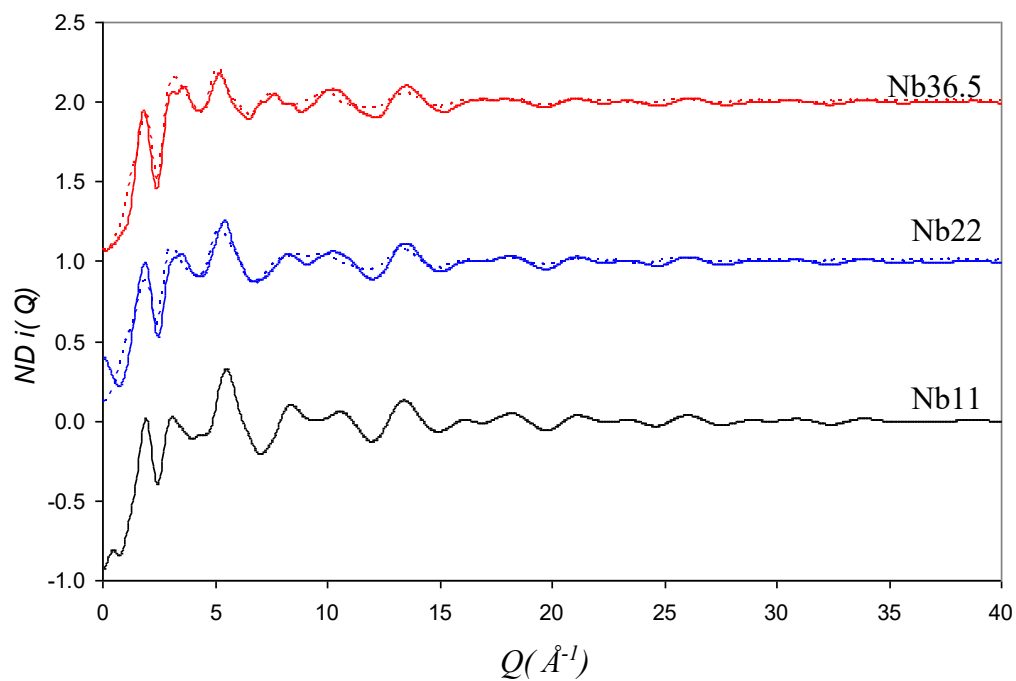
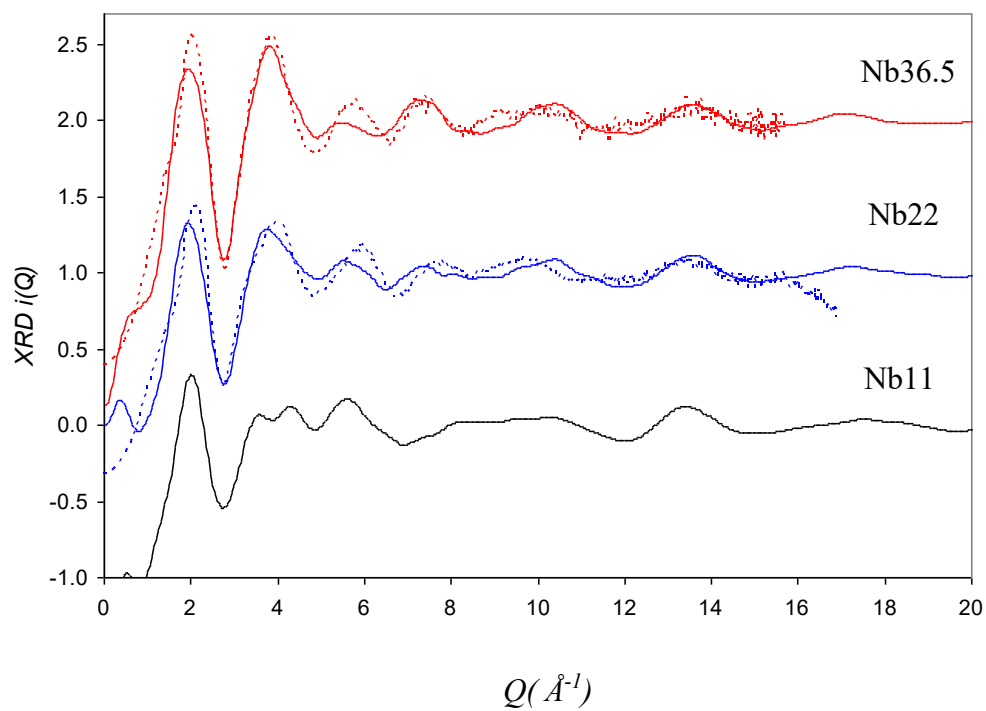


Figure 5: The Q -space interference function, $i(Q)$, for model results (solid lines) in comparison with the experiment (dashed line) from X-ray (top) and neutron diffraction (bottom). Each graph has been shifted by 1 for clarity.

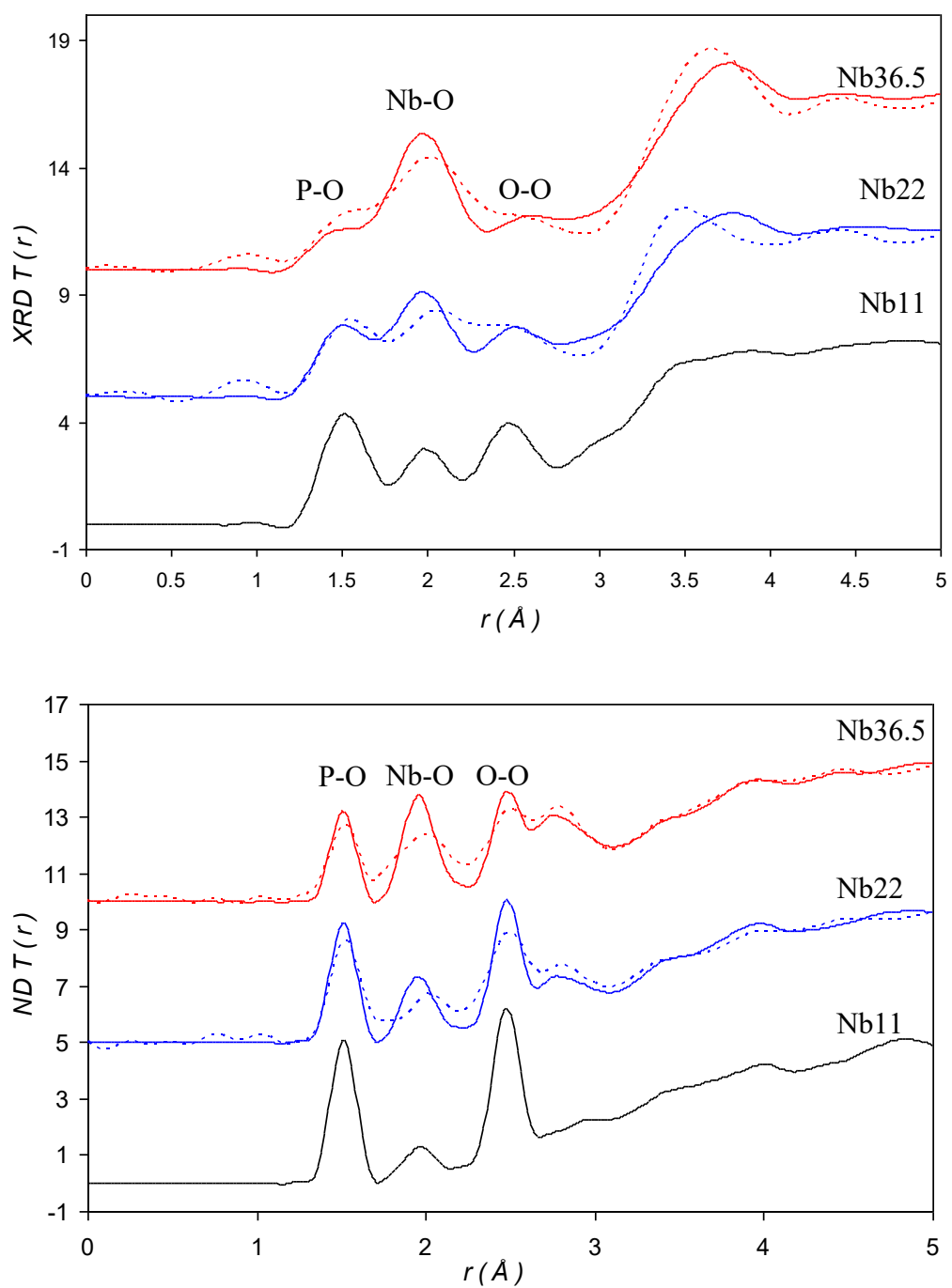


Figure 6: The total correlation function $T(r)$, for the model results (solid lines) in comparison with the experiment (dashed line) from X-ray (top) and neutron diffraction (bottom). Each graph has been shifted by 5 for clarity.

5. Discussion

As expected the models consist of a network of PO_4 tetrahedra with an average bond distance of $R_{\text{PO}} = 1.51 \text{ \AA}$ with P-O-P bond angles of $\sim 109.8^\circ$. Based on the results in Table 4, there is no appreciable variation in the P-O bond distances compared to those in the models group 1. According to the diffraction and NMR results [15], boron is predominantly coordinated to four oxygen atoms at low Nb^{5+} concentration. However, as the Nb concentration increases there is a noticeable shift to three-fold coordinated boron as confirmed through the shortening of the B-O bond length which agrees well the models results. The Nb is coordinated to six oxygen atoms with a mean bond distance of $\sim 1.96 \text{ \AA}$. This is consistent with the XRD and ND experiment and the vibrational spectroscopy features associated with NbO_6 octahedra [15]. A fourth type of cation-oxygen bond present in the structure is the Na-O correlation which is typically to be found in $2.30\text{--}2.42 \text{ \AA}$. Wetherall et al [15] reported that Na is surrounded by on average 3.4 oxygen atoms, this value from experiment is expected erroneous as Na-O distance completely overlaps with the O-O peak. Overall the agreement between the models and the experimental results [15] is acceptable for such a complex system.

The results summarized in Table 7 agree well with the vibrational spectroscopy results which confirm the presence of both P-O-P links and of isolated PO_4 units. However, the common negative aspect of MD models is a broad Q^n distribution about the average value. The decrease in P-P coordination number associated with increasing Nb content is due to the reduced network connectivity of P-O-P confirmed in Figure 4. This is clear evidence of the depolymerisation of the borophosphate network as Nb levels increase. Table 6 indicates an increase in the P links to other network formers B or Nb, and therefore, an increase of Q^0 at the expense of Q^1 , as the concentration of Nb is increased.

According to ^{31}P NMR results [34], there are chemical shifts of +10 ppm relative to a normal Q^n species if one of the O_b is linked to a network former other than P, such as B or Nb. This chemical shift can be used to assign PO_4 units as either $\text{P}^2_{(1)}$, $\text{P}^2_{(2)}$, or $\text{P}^3_{(3)}$. Therefore, a typical PO_4 unit has zero or one bridging oxygen to another phosphate unit and one, two or three bridging oxygen to either B or Nb. The former was proved by the model through the P-P coordination numbers given in Table 6. On the other hand, the P-Nb and P-B coordination numbers are increased with the

addition of Nb form a total of ~ 1 in Nb11 model to ~ 3.2 in Nb36.5 model as shown in Table 6. This agrees well with the three possibilities of $P^{m(n)}$ from the NMR results. At low Nb content, Nb is likely to coordinate to another cation rather than Nb. As the concentration increases the Nb begins to have more Nb neighbours [18]. This can be reinforced through the models by looking to Nb-Nb linkages between the Nb octahedra. The models show that the average coordination numbers of Nb-Nb increased from 1.09 to 3.14 with increasing Nb level.

The ^{11}B NMR chemical shifts were assigned as $B^4_{(4)}$ indicating an isolated BO_n polyhedron. Table 4 shows the shortening of the B–O bond length with increasing Nb content corresponding with the decrease in the coordination towards 3. Additionally, Table 6 shows that at low Nb content, B is more likely to coordinate with P rather than Nb, whereas the B-Nb linkage increases with the addition of Nb.

In the previous experimental work [15], the results were interpreted in terms of a detailed picture of the preferred distribution of B, P, Na and Nb ions, as shown in Figure 7. This picture can be compared with the results from MD modelling for Nb11 model, as reported in Table 6. Wetherall et al [15] concluded that the balance of bond valence at bridging oxygen atoms play an important role in the connectivity in this structure. The balance of bond valence at bridging oxygen gives a preference for $P \cdot \cdot B/\text{Nb}$ linkages over $P \cdot \cdot P$ linkages [15]. For example, based on their experimental coordination numbers the average bond valence of P–O, B–O and Nb–O are predicted to be 1.25, 0.75, 0.83, respectively, using the Brese and O’Keeffe Equation [35]. Therefore, the $P \cdot \cdot B/\text{Nb}$ linkages provide well-balanced bond valence at bridging oxygen atoms, because the sum of the P–O and the B–O or Nb–O bond valences is approximately equal to the bridging oxygen valence of 2^- , while the $P \cdot \cdot P$ and $B/M \cdot \cdot B/\text{Nb}$ linkages have less balanced bond valence.

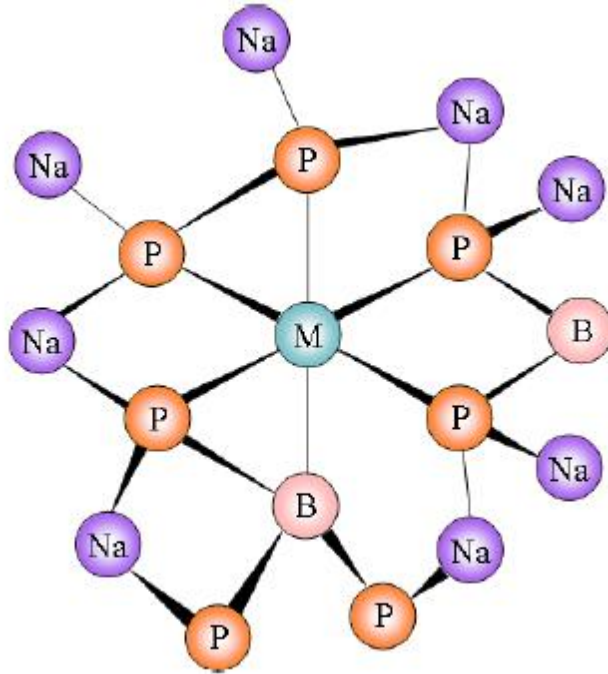


Figure 7: A model of the connectivity at low Nb content, the oxygen atoms are not shown but would be positioned on the lines between cations [15].

Based on the ratio of Na: B: P: Nb which is approximated as 5: 1: 4.5: 1, and assuming coordination numbers of 5, 4, 4 and 6, respectively, at low Nb content, Wetherall et al [18] suggested the following picture (Figure 5.18) of the structure at low Nb content:

- The typical connectivity of B could be described as $3 \text{ B} \cdot \cdot \text{P}$ and $1 \text{ B} \cdot \cdot \text{Nb}$ linkages. At low Nb the Nb11 model shows that B is coordinated to an average of 0.8 B, 1.29 P and 1.07 Nb.
- The typical connectivity of P would be $0.67 \text{ P} \cdot \cdot \text{B}$, $0.33 \text{ P} \cdot \cdot \text{P}$, and $1.11 \text{ P} \cdot \cdot \text{Nb}$ linkages. At low Nb the Nb11 model shows that P is coordinated to an average 1.53P, 0.28B and 0.75Nb.
- Each Nb was described as having $1 \text{ Nb} \cdot \cdot \text{B}$ and $5 \text{ Nb} \cdot \cdot \text{P}$ linkages. The preference of Nb to coordinate to P rather than B was proven in Table 5.17.

- According to the model results given in Table 5.17 the Nb-Nb coordination number is only 1 at low Nb content however, it increases with the addition of Nb content
- The coordination of P would be completed with 1.9 bonds to O_{nb}, and these O_{nb} have to be coordinated to the network modifier Na.

6. Conclusion

All borophosphate glasses confirm networks the tetrahedral structure. Both Nb and Na play the role of modifier. Modelling the structure of sodium borophosphate glass containing niobium gave fair agreement with the experimental results reported by Wetherall et al. Nb octahedra prefer to be isolated at low Nb content, and connected to other NbO₆ octahedra at higher Nb content.

Declaration

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

7. References

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Authors Contributions

Bushra ALHasni performed the simulations, analysed the results, and wrote the manuscript. Gavin Mountjoy interpreted the results and reviewed the manuscript.

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