Network structure of Mo-oxide glasses

M Fabian¹,², E Svab³, M Milanova³ and K Krezhov⁴

E-mail: fabian.margit@energia.mta.hu

¹Centre for Energy Research, 1121 Budapest, Konkoly-Thege st. 29-33, Hungary
²Wigner Research Centre for Physics, 1121 Budapest, Konkoly-Thege st. 29-33, Hungary
³Institute of General and Inorganic Chemistry, 1113 Sofia “Acad. G. Bonchev” str., bld. 11, Bulgaria
⁴Institute for Nuclear Research and Nuclear Energy, 1784 Sofia, 72 Tzarigradsko Chaussee, Bulgaria

Abstract. The structure of molybdate glasses have been investigated by neutron and high-energy X-ray diffraction coupled with Reverse Monte Carlo (RMC) simulation technique. From the modelling the partial atomic correlation functions \( g_{ij}(r) \), the coordination number distributions \( CN_{ij} \) and bond angle distributions have been revealed. For binary 90MoO\(_3\)-10Nd\(_2\)O\(_3\) glass composition the fraction of MoO\(_2\)/MoO\(_6\) was 0.55/0.25. Three type of ternary system have been studied, where the most important structural units was authenticated. For MoO\(_3\)-Nd\(_2\)O\(_3\)-B\(_2\)O\(_3\) sample mixed MoO\(_3\)-BO\(_4\) and MoO\(_4\)-BO\(_3\) linkages form pronounced intermediate-range order. In case of MoO\(_3\)-ZnO-B\(_2\)O\(_3\) series the BO\(_4\) and BO\(_3\) units are linked to MoO\(_4\) and/or ZnO\(_4\), forming mixed MoO\(_2\)-BO\(_4\)(BO\(_3\)), MoO\(_4\)-ZnO\(_4\) and ZnO\(_2\)-BO\(_4\)(BO\(_3\)) bond-linkages.

1. Introduction

Rare-earth molybdates display a variety of crystal and amorphous structures and possess useful electro-physical, optical, high ion and electron conductivity properties derived from the parent oxide La\(_3\)MoO\(_8\) [1,2]. The molybdates LiLn(MoO\(_3\))\(_2\), Ln=Nd, Pr, Ho are excellent LN-doped laser hosts [3].

Zinc boromolybdate materials are known as low melting dielectric materials and they have high potential in several applications, due to their stable and unique structure with favourable optical properties. In contrast to the most molybdates with relatively well-characterised crystalline and magnetic structures, e.g. [4-7], the preparation and structural information on amorphous molybdate systems is not ample. Glass formation in molybdate systems, containing different kind of oxides, has been examined by our team as a part of long term academic projects, concerning non-traditional glass forming systems [8-10]. The phase diagram for several oxides, MoO\(_3\)-Nd\(_2\)O\(_3\)-B\(_2\)O\(_3\) was set up [9] and the basic structural and optical characteristics were investigated by XRD, DTA, SEM, UV-VS spectra and IR spectroscopy [10].

The purpose of this work is to verify the competition for the glass network formation between non-traditional network formers - MoO\(_3\), ZnO - and to get a deeper insight into the structural network characteristics of new series of molybdates containing modifiers Nd\(_2\)O\(_3\), MgO and classical glass former B\(_2\)O\(_3\). For this study three new amorphous sample series of the glassy MoO\(_3\)-Nd\(_2\)O\(_3\)-MgO, MoO\(_3\)-Nd\(_2\)O\(_3\)-B\(_2\)O\(_3\) and MoO\(_3\)-ZnO-B\(_2\)O\(_3\) system have been prepared by rapid quench technique.
In this paper, the structure of molybdate glasses is investigated using neutron and high-energy X-ray diffraction experiments, and for structure modeling the Reverse Monte Carlo (RMC) computer simulation technique [11] was applied. We expect to obtain new structural data, especially on the characteristics of the partial atomic pair correlation functions, the first neighbor atomic distances, coordination numbers and network former units and their linkages.

2. Experimental details and methods

2.1. Samples

The samples with the nominal composition 90MoO$_3$-10Nd$_2$O$_5$ (hereafter referred to as Mo90Nd10), ternary 80MoO$_3$-15Nd$_2$O$_5$-5MgO (Mo80Nd15Mg5), 75MoO$_3$-12.5Nd$_2$O$_5$-12.5MgO (Mo75Nd12.5Mg12.5), 50MoO$_3$-25Nd$_2$O$_5$-25B$_2$O$_3$ (Mo50Nd25B25), 40MoO$_3$-30Nd$_2$O$_5$-30B$_2$O$_3$ (Mo40Nd30B30) and 20MoO$_3$-30Nd$_2$O$_5$-50B$_2$O$_3$ (Mo20Nd30B50); 30MoO$_3$-50ZnO-20B$_2$O$_3$ (Mo30Zn50B20), 20MoO$_3$-50ZnO-30B$_2$O$_3$ (Mo20Zn50B30) and 10MoO$_3$-50ZnO-40B$_2$O$_3$ (Mo10Zn50B40) (mol%) have been prepared from reagent grade powders (B$_2$O$_3$, MoO$_3$, Nd$_2$O$_5$, ZnO, MgO) melted in a platinum crucible at 1200-1300°C for 30 min. B$_2$O$_3$ enriched with $^{11}$B isotope (99.6%) has been used in order to avoid the high neutron absorption cross section of the $^{10}$B isotope. The melting temperature was limited to 1300°C taking into account the volatility of the components. The glasses were obtained by pouring the melts onto an iron plate and by pressing with another iron plate.

2.2. Neutron and X-ray diffraction experiments

Neutron diffraction (ND) data have been obtained on the two-axis ‘PSD’ diffractometer at the 10 MW Budapest research reactor ($\lambda_o=1.068$ Å) [12], on the time-of-flight ‘HIPD’ instrument [13] at the LANSCE pulsed neutron source (for Mo-Nd-Mg-O samples) and on the ‘7C2’ diffractometer at the Orphée reactor of the LLB-CEA-Saclay ($\lambda_o=0.726$ Å) [14] (for the Mo-Nd-B-O and Mo-Zn-B-O samples series). Glass powders were contained in a cylindrical vanadium sample holder of 8 mm (PSD, 7C2) and 10 mm (HIPD) diameter for the three types of experiments. The structure factors, $S(Q)$, were evaluated from the raw experimental data using the programme packages available at the facilities. The $S(Q)$’s were obtained in the $Q=0.45-9.8$ Å$^{-1}$ (PSD), $Q=0.2-15.5$ Å$^{-1}$ (7C2) and $Q=1.5-35$ Å$^{-1}$ (HIPD) experiments. The agreement between the corresponding $S(Q)$ data was within 1% in the overlapping $Q$ range. The statistics of the PSD data is excellent at relatively low $Q$ values, while the statistics and the information content of the 7C2 and HIPD data is unique above 8 Å$^{-1}$. Therefore the $S(Q)$ patterns were combined by normalizing the PSD data to the 7C2 and HIPD data sets in the 4-8 Å$^{-1}$ interval by the least-squares method, and the average values of the two spectra were used for further data treatment, while for $Q>4$ Å$^{-1}$ the PSD data and for $Q>8$ Å$^{-1}$ the 7C2 and HIPD data were used.

The high-energy X-ray diffraction (XRD) measurements were carried out at the BW5 experimental station [15] at HASYLAB, DESY for Mo-Nd-O and Mo-Nd-Mg-O samples. The powdered samples were filled into quartz capillary of 2 mm in diameter. The energy of the radiation was 109.5 keV. Raw data were corrected for detector dead time, background, absorption, and variations in detector solid angle. The synchrotron X-ray radiation makes it possible to reach diffraction data up to high-$Q$ values. For the Mo-Nd-B-O samples X-ray diffraction studies were performed at the beam line ID22 at ESRF. The fine powdered samples were filled into kapton capillary tubes of 1 mm in diameter and measured at room temperature. The energy of the radiation was 70.8 keV. The X-ray $S(Q)$ data were obtained with a good signal-to-noise ratio up to $Q_{\text{max}}=25$ Å$^{-1}$ at BW5 station and up to $Q_{\text{max}}=22$ Å$^{-1}$ at ID22, for higher $Q$-values the experimental data proved to be noisy.

The overall run of the curves for the two radiations is fairly different, because of the differences in the weighting factors, $w_{ij}$ of the partial structure factors, $S_{ij}(Q)$:

$$S(Q) = \sum_{ij} w_{ij} S_{ij}(Q)$$  \hspace{1cm} (1)
\[ w_{ij}^{ND} = \frac{c_i c_j b_i b_j}{\sum_{i,j} c_i b_j} \]  
\[ w_{ij}^{XD}(Q) = \frac{c_i c_j f_i(Q) f_j(Q)}{\sum_{i,j} c_i f_j(Q)} \]

(2)  

(3)

where \( c_i, c_j \) are the molar fractions of the components, \( b_i, b_j \) the coherent neutron and \( f_i(Q), f_j(Q) \) the X-ray scattering amplitudes, and \( k \) is the number of elements in the sample. Note, that the neutron scattering amplitude is constant [16], while the X-ray scattering amplitude is Q-dependent [17].

3. Reverse Monte Carlo simulations

Reverse Monte Carlo modelling have been performed using the RMC++ code [11], starting with a disordered atomic configuration. The RMC minimizes the squared difference between the experimental \( S(Q) \) and the calculated one from a 3D atomic configuration. The RMC algorithm calculates the one-dimensional partial atomic pair correlation functions \( g_{ij}(r) \), and they are inverse Fourier transformed to calculate the partial structure factors, \( S_{ij}(Q) \).

For the RMC starting model disordered atomic configuration was built up with a simulation box containing 10,000 atoms. The density values were 0.0733, 0.0668, 0.0670 atoms·Å\(^{-3}\) for Mo90Nd10, Mo80Nd15Mg5, Mo75Nd12.5Mg12.5 samples, respectively, and the corresponding RMC half-box lengths were 25.739, 26.548 and 26.522 Å. The density values were 0.0683, 0.0684 and 0.0692 atoms·Å\(^{-3}\) were used for the Mo50-Nd25-B25, Mo40-Nd30-B2O30 and Mo20-Nd30-B50 samples, respectively, and the corresponding RMC half-box lengths were 26.353, 26.340 and 26.238 Å. The density data 0.087, 0.081 and 0.076 atoms·Å\(^{-3}\) and half-box values \( r_{max} = 24.30 \) Å, 24.90 Å and 25.43 Å for the Mo10-ZnO50-B40, Mo20-Zn50-B30 and Mo30-Zn50-B20 samples, respectively.

In order to generate a realistic structural model, minimum atom-atom distances were chosen to avoid an unphysical overlapping of the atoms and B atoms were imposed to be trigonally and tetrahedrally coordinated. It is reasonable to suppose that boron atoms are surrounded both by three-coordinated and four-coordinated oxygen atoms, forming trigonal BO\(_3\) and tetrahedral BO\(_4\) units as reported for binary neodymium borate glasses [20], for ternary rare-earth boromolybdate MoO\(_3\)-Nd(La)\(_2\)O\(_3\)-B\(_2\)O\(_3\) [9,10], for B\(_2\)O\(_3\)-Bi\(_2\)O\(_3\)-MoO\(_3\) glass [21], similarly, as for binary alkali borate glasses [22 and references therein]. For the starting cut-off distances we have used the characteristic values for B-O 1.2 Å, Mo-O 1.6 Å, Nd-O 2.0 Å, Zn-O 1.9 Å and O-O 2.3 Å. Several RMC runs have been completed by modifying the cut-off distances in the way, that the results of each run have been carefully checked to obtain reliable data for each \( g_{ij}(r) \) and coordination number distributions, \( CN_4(n) \). The convergence of the RMC calculations was good and the final \( S(Q) \)s matched very well the experimental ones. (see figure 1).
The partial atomic pair correlation functions, $g_{ij}(r)$, have been revealed from RMC simulation with a good reproducibility and acceptable statistics. The most important oxygen-linked $g_{i-O}(r)$ and coordination number distributions are shown in figure 2.

**Figure 2a.** O-linked partial atomic pair correlation functions obtained from the RMC modelling for the: Mo90Nd10 (black square), Mo80Nd15Mg5 (orange circle) and Mo75Nd12.5Mg12.5 (red triangle).

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Average partial coordination numbers, Table 2.

Oxygen-linked atomic distances, Table 1.

**Figure 2b.** O-linked partial atomic pair correlation functions obtained from the RMC modelling for the: Mo50Nd25B25 (blue square), Mo40Nd30B30 (magenta circle) and Mo20Nd30B50 (green triangle).

**Figure 2c.** O-linked partial atomic pair correlation functions obtained from the RMC modelling for the: Mo30Zn50B20 (blue square), Mo20Zn50B30 (red circle) and Mo10Zn50B40 (green triangle).

**Table 1.** Oxygen-linked atomic distances, $r_{ij}$ (Å).

| Sample       | Mo-O (±0.02) | Nd-O (±0.05) | Zn-O (±0.01) | B-O (±0.02) | Mg-O (±0.1) | O-O (±0.1) |
|--------------|--------------|--------------|--------------|-------------|-------------|------------|
| Mo90Nd10     | 1.80/2.0     | 2.0/2.8      | -            | -           | -           | 2.3/2.8    |
| Mo80Nd15Mg5  | 1.80         | 2.1/2.8      | -            | -           | 1.8         | 2.45/2.8   |
| Mo75Nd12.5Mg12.5 | 1.80     | 2.1/2.9      | -            | -           | 1.8/2.1     | 2.4/2.8    |
| Mo50Nd25B25  | 1.80/2.0     | 2.4/2.8      | -            | 1.45        | -           | 2.35/2.8   |
| Mo40Nd30B30  | 1.75/1.95    | 2.4/2.9      | -            | 1.42        | -           | 2.3/2.8    |
| Mo20Nd30B50  | 1.75         | 2.4/2.9      | -            | 1.40        | -           | 2.3/3.0    |
| Mo30Zn50B20  | 1.74         | -            | 1.98         | 1.39        | -           | 2.35/2.80  |
| Mo20Zn50B30  | 1.72         | -            | 1.97         | 1.39        | -           | 2.35/2.90  |
| Mo10Zn50B40  | 1.72         | -            | 1.97         | 1.38        | -           | 2.35/2.95  |

**Table 2.** Average partial coordination numbers, $CN_{ij}$ (atom).

| Sample       | Mo-O (±0.2) | Nd-O (±0.1) | Zn-O (±0.5) | B-O (±0.5) | O-O (±0.5) |
|--------------|-------------|-------------|-------------|------------|------------|
| Mo90Nd10     | 4.9         | 4.3         | -           | -          | 8.0        |
| Mo80Nd15Mg5  | 4.2         | 3.1         | -           | -          | 6.9        |
| Mo75Nd12.5Mg12.5 | 4.0  | 3.1         | -           | -          | 6.2        |
| Mo50Nd25B25  | 4.2         | 5.1         | -           | 3.35       | 5.5        |
| Mo40Nd30B30  | 4.0         | 5.0         | -           | 3.2        | 5.2        |
| Mo20Nd30B50  | 3.5         | 4.9         | -           | 3.1        | 4.4        |
| Mo30Zn50B20  | 3.9         | -           | 4.0         | 3.1        | 5.4        |
| Mo20Zn50B30  | 3.9         | -           | 3.9         | 3.2        | 5.1        |
| Mo10Zn50B40  | 3.9         | -           | 3.8         | 3.3        | 5.0        |
The corresponding first neighbour distances are presented in table 1 and the average CN_{1,O} in table 2. In the studied system the results obtained from RMC modelling have shown significant correlations between several second neighbour atom pairs, as it is shown in figure 3. This is important, as far as the analysis of these results may give useful information on the linkage of the basic structural units forming the network structure. The second neighbour partial distributions are collected in figure 3.

Figure 3. Second neighbour partial atomic pair correlation functions obtained from the RMC modelling for the molydate glasses.

4. Discussion
In the present study for the Mo-O atom pair correlations a well-defined first neighbour distance is obtained at 1.80±0.05 Å, and the course of the curves is practically the same for all investigated samples. The observed Mo-O distance is somewhat greater than the 1.75(5)Å distance reported for glassy 90MoO_3-10Nd_2O_3 from EXAFS measurements [23], and shows similarity to the Mo-O 1.73-1.82Å distances in crystalline LaBMoO_6 [24] and in Nd_2O_3-MoO_3 [5]. For the Mo-Nd-B-O samples the Mo-O correlation functions show a sharp peak at an average distance of 1.75±0.05 Å, with a half-width value of ~0.04 Å, while a significantly smaller “sub”-peak appears at an average distance of 1.95±0.05 Å. The position of both the main peak and the sub-peak doesn’t show any concentration dependence within the limit of error. In case of Mo-Zn-B-O samples the Mo-O distance shows a slight decrease from 1.74 Å to 1.72 Å with decrease of molybdenum content. This is an indication on the formation of stable Mo-O network structure.

The Nd-modifier shows characteristic Nd-O first neighbour distance at 2.1Å, and a next one at 2.8 Å for the binary Mo90Nd10, while for the other compositions the first neighbour distance shifts to slightly higher distances 2.4-2.8(9) Å. The intensity decreases and the peak is less characteristic inspite of the increased Nd-concentration in the ternary samples. The reason for this result may be in the more complicated network due to the increased number of constituent components. The small peak
at 2.85 Å seems to be reproducible, however, the peak position agrees with the second O-O distance, thus its origin may be artificial. The Nd-O distances reported in the literature are somewhat greater than our results, i.e. 2.51-2.73 Å in glassy MoO$_3$-Nd$_2$O$_3$ [8], 2.33-2.5 Å in crystalline Nd$_2$O$_3$-MoO$_3$ [5], 2.24-2.32 Å in Y$_{2-x}$Nd$_x$Mo$_9$O$_{15}$ [25]. The Zn-O distance appears at significantly higher value, at 1.97 Å which is in good agreement with the results obtained for other glasses with ZnO ($r_{Zn-O}=1.93$-1.95 Å [26], 1.83-1.91 Å [27], 1.94-1.97 Å [28]). The B-O distribution function shows a relatively broad first neighbour distance at 1.40±0.05 Å with a half-width value of 0.25 Å, is usually the case for B-O network [18, 22]. In the Mo-Zn-B-O samples the B-O first neighbour distance shows slight concentration dependence, it changes from 1.38 Å to 1.39 Å with increasing boron content, which is in good agreement with previous result obtained for Mo-Nd-B-O glass.

In the high Mo-containing binary Mo$_90$Nd$_{10}$ sample the average number of oxygen atoms around Mo is 4.9±0.2 atoms. We have investigated the possibility of a mixed network, containing both MoO$_4$ and MoO$_6$ units, by RMC simulation. If we suppose that MoO$_4$ units similarly to the crystalline LaBMoO$_6$ [24], Nd$_2$O$_3$-MoO$_3$ [5] and usually this is the case for molybdate crystals. For glassy molybdate network the presence of MoO$_4^2$ units were reported [9, 10, 21], while the formation of MoO$_6$ units was also observed, they are present in the network. In case of binary system it would mean that 55% of the Mo atoms are 4-fold oxygen coordinated, while 25% are 6-fold coordinated, while the rest 20% are in 3- and 5-fold coordinated states, with an error about 5%. Taking into consideration the $g_{Mo-O}(r)$ distribution, we can establish that the shorter distance at 1.8 Å can be attributed to the MoO$_4$ units, while in addition two further oxygen neighbours appear at a longer 2.0 Å distance forming MoO$_6$ units. According to table 2, with decrease of Mo content the number of oxygen neighbours slightly decreases to 4.0 atoms. For the Mo-Nd-Mg-O, Mo-Nd-B-O and also for the Mo-Zn-B-O ternary samples the average coordination number, as calculated from the RMC modeling, is close to 4. In case of ternary systems distortion of the tetrahedral MoO$_4$ units can not be excluded.

The average number of oxygen neighbours of the modifier Nd is 4.3 atoms for both the binary Mo$_90$Nd$_{10}$ and for the boron-containing ternary sample, while it is significantly smaller for the Mg containing samples, 3.1 atoms. The reason may be that Mg is also a modifier, which plays a similar role like Nd, increasing the number of non-bridging oxygen (NBO) atoms.

The B-O coordination number distributions contain both 3- and 4-fold oxygen coordinated boron atoms. The average coordination number slightly decreases from 3.3 to 3.1 atoms with increasing boron content in case of Mo-Nd-B-O system (see table 2). The fraction of BO$_3$ and BO$_4$ to the total number of {BO$_3$+BO$_4$} is an important structural characteristics. It was found that the relative number of 3- and 4-fold coordination depends on the boron concentration. With increasing boron content the relative number of BO$_3$ units is increasing, while the number of BO$_4$ is decreasing. For 50MoO$_3$-25Nd$_2$O$_3$-25B$_2$O$_3$ sample ~70% of B-atoms are 3-coordinated, while ~30% are 4-coordinated, the average coordination number is 3.3 atoms; for 40MoO$_3$-30Nd$_2$O$_3$-30B$_2$O$_3$ glass ~77% of B-atoms are 3-coordinated, while ~23% are 4-coordinated, the average coordination number is 3.2 atoms; for 20MoO$_3$-30Nd$_2$O$_3$-50B$_2$O$_3$ sample ~87% of B-atoms are 3-coordinated, while ~13% are 4-coordinated, the average coordination number is 3.1 atoms. With increasing B$_2$O$_3$ and Nd$_2$O$_3$ content, the number of BO$_3$ trigonal units increases, while the number of BO$_4$ units decreases, this is an indication, that conversion of BO$_3$ to BO$_4$ takes place.

Interesting B-O coordination number distributions have been revealed for the Mo-Zn-B-O series. The ratio of BO$_3$ and BO$_4$ units shows concentration dependence on B$_2$O$_3$ content. For the low boron content sample the relative number of 3-fold coordinated boron atoms is significantly higher than that for the higher boron content samples. In consequence, the average $CN_{B-O}$ slightly increases with increasing B$_2$O$_3$. We discussed above the relative number of BO$_3$ and BO$_4$ units, but we have to keep in mind, that complex borate glasses cannot be viewed as a simple network built only from BO$_3$ triangles and BO$_4$ tetrahedrals, but usually they consist of relatively large structural units, such as boroxol, pentaborate, triborate and diborate groups [29,30]. However, a possible analysis of such kind of superunits is out of the scope the present study.
The O-O average coordination number is 8 atoms for the 2-component Mo90Nd10 sample, which is the highest among the investigated samples. The average O-O coordination number reduces to 6 or 5 atoms for the samples with increasing number of contributing components, which may be the consequence of mixed structural units.

The linkage of the network former units is an important point. The RMC modelling also provides information on the second coordination sphere. The basic question is, whether the linkage of the basic structural units show any correlation or not? The question may be raised, whether the Mo-based network is separated from the B-based one, or are there any separated MoO4 units or not? We have calculated the second neighbour correlations by RMC, and significant correlations have been revealed, as it is shown in figure 3.

The analysis of the metal-metal and boron-metal pair correlation functions show pronounced correlations, the corresponding atomic pair distances are shown in figure 3. We can establish as main points, that the pronounced Mo-Mo correlation can be interpreted as linkage between the MoO4 units for all samples. The shortest second neighbour distances are obtained for Mo-B 2.85 Å, Zn-B 2.85 Å and Nd-B 3.1 Å, which indicate appearance of mixed linkages. These results indicate the existence of a pronounced intermediate-range ordering. Medium range order was established formed by mixed MoO4-B4O3 and MoO4-BO4 linkages besides the pronounced Mo-Mo second neighbour correlations.

We have calculated the three-particle bond-angle distributions using the final atomic configuration of the RMC algorithm, plotted both as the function of \( \cos(\Theta) \) (scale below) and \( \Theta \) (upper scale), where \( \Theta \) represents the actual bond angle. Figure 4 shows the distributions for the network former atoms (for Mo-Zn-B-O samples): Mo-O-B, B-O-Zn and Mo-O-Zn.

![Figure 4. Three-particle bond-angle distributions obtained from RMC simulation for Mo30Zn50B20 (blue square), Mo20Zn50B30 (red circle) and Mo10Zn50B40 (green triangle).](image)

For the Mo-O-B and Mo-O-Zn the peak positions are at 149±3° and 104±5°, respectively, which are very close values to the ideal tetrahedral configuration. B-O-Zn distribution also show a close link between the boron and zinc units. The addition of a modifier initially converts BO4 triangles into BO3 tetrahedra, increasing coordination number and strengthens the network. We suppose that the network is formed by BO3 and BO4 organized into superstructure units, and linked to MoO4 or ZnO4, forming in this manner mixed bond-linkages.

In the these systems the oxygen centred coordination number distributions show that most of Mo atoms favour to be connected through an oxygen to Zn and B atoms, and the majority of the Zn also prefer to be linked to B or Mo forming in this way \( ^4\text{Mo-O} \), \( ^3\text{Mo-O} \), \( ^4\text{B-O} \), \( ^3\text{B-O} \), \( ^4\text{Zn} \), \( ^3\text{Zn} \) linkages.

5. Conclusions

Molybdate glasses have been prepared by melt quenching technique, and the network structure was investigated by neutron and high-energy X-ray diffraction. For data evaluation the RMC simulation technique was applied to obtain a possible 3-dimensional network configuration, which is consistent with the experimental data. From the RMC modelling the partial atomic correlation functions \( g_{ij}(r) \) and the coordination number distributions \( CN_{ij} \) have been revealed. Formations of MoO4 units were
established with 1.75/1.80 Å Mo-O distances. In the binary glass MoO₄ (55%) and MoO₆ (25%) structural units were revealed. In ternary systems mainly MoO₄ units are present, and with decreasing MoO₃ concentration, the ratio of MoO₆ units roughly decreases. For the B-containing ternary glasses B-O first neighbour distance was obtained at 1.40 Å, the B-O network is formed by BO₃ and BO₄ groups. ZnO proved to be a network former, not a modifier as it is often reported in the literature for similar systems. From the analyses of the obtained structural parameters we have concluded that the glassy network is formed by trigonal BO₃ and tetrahedral BO₄, MoO₆, ZnO₄ groups. Concentration dependence was found for the BO₄/BO₃ fraction, it increases with increasing B₂O₃ content. We have concluded that the network is formed by organization of BO₃ and BO₄ groups. The BO₃ and BO₄ units are linked to MoO₄ or ZnO₄, forming mixed [⁴]Mo-O-[¹][⁴]B, [⁴]Mo-O-[⁴]Zn, [³][⁴]B-O-[⁴]Zn bond-linkages. Significant medium-range order exists up to ~7 Å.

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