

Investigation of short-range atomic order in glasses from the $\text{MoO}_3\text{-TeO}_2$ system

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Short-range atomic order in the $\text{MoO}_3\text{-TeO}_2$ glassy system has been studied by the neutron diffraction method. With increase of the amount of MoO_3 from 20 to 50 mol%, a sequential transition $4 \rightarrow (3 + 1) \rightarrow 3$ of the coordination state of tellurium with respect to oxygen was observed. Throughout this process, a formation of MoO_5 and MoO_4 groups was detected. The interpretation of the experimental radial distribution functions was performed by comparison with quasi-crystalline model curves (structure diffusion model).

1. Introduction

Multicomponent oxide catalysers based on TeO_2 and MoO_3 are of interest because of their selective and highly oxidizing catalytic properties [1-5]. The phase diagrams [6, 7] are known, as well as the crystalline structures of the tellurium molybdates [8-10]. Data are published about the glass-formation tendency and the properties of the glasses in the binary $\text{MoO}_3\text{-TeO}_2$ and tricomponent $\text{MoO}_3\text{-TeO}_2\text{-V}_2\text{O}_5$ systems [11]. The constituents MoO_3 and TeO_2 belong to the conditional glass-formers, but separately their melts can be fixed in a glassy state on rapid cooling in small volumes. Melts of the binary $\text{MoO}_3\text{-TeO}_2$ system, however, are easily fixed in a glassy state at normal cooling rates. The glass-formation limits in the system are in the range of 12.5 to 58.5 mol% MoO_3 * [12].

The present investigation aims to study the structural arrangement in these glasses and the structural influence of the initial constituents on the short-range order in the $\text{MoO}_3\text{-TeO}_2$ glassy system.

The tellurium molybdenum oxide glass structure is not sufficiently well studied. There are only X-ray diffraction data published [13] which barely reflect the distribution of oxygen atoms. The large O^{2-} ions ($R = 0.136$ nm) form the anion network of the glass and exhibit a determining influence on the cation locations of the glass-former or the modifier. The neutron diffraction method used here eliminates the strong dependence of the intensity of scattered X-rays on the atomic numbers of the elements. The neutron coherent scattering amplitudes of nuclei are 0.58, 0.545 and $0.69 (\times 10^{-12})$ cm for oxygen, tellurium and molybdenum respectively. Because of their closeness the contribution of the partial radial distribution functions to the total radial distribution function

(RDF) will be of the same order of magnitude. For multicomponent glasses such as those investigated here, a diffraction experiment is not sufficient for the unambiguous determination of partial RDF. For this reason, in interpreting the total RDF we used a model approach based on the structure diffusion model (SD model) [14].

2. Experimental procedure

2.1. Sample synthesis

Raw materials (MoO_3 and TeO_2) of p.a. purity were used. The sample preparation technology is described elsewhere [15]; their compositions and densities are listed in Table I. The samples were not annealed or subjected to any other thermal treatment, following their synthesis. The compositions were chosen on the basis of the following considerations:

(i) TM1 makes it possible to follow the effect of MoO_3 on the short-range atomic order of the glass-former and on the oxygen surroundings characteristic of the tellurium atom. A comparison can also be made with glasses previously investigated by us, containing P_2O_5 [16], Li_2O [17], WO_3 [18] and ZnO [19].

(ii) TM2 is isoplait with the geometrical point of MoTe_2O_7 and enables one to correlate it with the crystalline structures of $\alpha\text{-TeO}_2$, MoO_3 and MoTe_2O_7 . The composition is located closely to the eutectic point of the system [6].

(iii) TM3 is near the upper boundary of the glass formation region, which provides a possibility to observe the equimolecular influence of the two components upon the glass structure—a phenomenon that is relatively non-typical for tellurite glassy systems.

* All compositions in this work are presented in molar percentages.

TABLE I Sample compositions and densities

Sample	Composition (mol %)		Density (g cm ⁻³)
	TeO ₂	MoO ₃	
TM1	80	20	5.28
TM2	66.7	33.3	4.95
TM3	50	50	4.70

TABLE II Positions of atomic density maxima

Sample	Position (nm)						
	P1	P2	P3	P4	P5	P6	P7
TM1	0.192	0.281	0.375	0.465	0.540	0.710	0.825
TM2	0.190	0.280		0.438	0.525	0.685	0.783
TM3	0.187	0.280	0.375	0.460	0.530	0.660 + 0.735	0.805

2.2. Experimental technique and conditions

The scattering curves $I(Q)$, where $Q = 4\pi \sin \theta/\lambda$, were obtained using the neutron diffractometer DN 520 in the IRT 2000 reactor, in Sofia, at $\lambda = 0.1061$ nm within the angular range $2\theta = 4$ to 115° . Scanning was performed with a constant step $\Delta Q = 1 \text{ nm}^{-1}$ to $Q_{\text{max}} = 100 \text{ nm}^{-1}$. The experimental diffraction data were smoothed out following the smooth-approximation method with an analytic function [20].

The same compositions were investigated by means of a TKSN400 spectrometer at the Nuclear Physics Institute, Rez-Prague using the θ - 2θ method within the range 5 to 84 nm^{-1} . The first coordination maximum on the experimental RDF thus obtained was not well expressed, due to considerably lower resolution. Independently the relative variations of RDF as a function of the composition were used for comparison in determining the positions and the coordination numbers (c.n.) of the atoms within the first coordination sphere.

3. Experimental results

The interference functions shown in Fig. 1 all have the appearance typical of glassy scatterers with maxima at 18, 29, 48.5 and $\sim 73 \text{ nm}^{-1}$. The light oxygen nuclei in the glasses give rise to an observable non-elastic scattering. For this reason the experimental data were corrected in relation to the presence of non-elastic and

multiple scattering, in accordance with [21]

$$f_p = \frac{m}{M} \left(\frac{kT}{2E_0} - \frac{Q^2}{Q_0^2} \right) + \left(\frac{m}{M} \right)^2 \left(\frac{1}{2} \frac{Q^2}{Q_0^2} + \frac{3}{8} \frac{Q^4}{Q_0^4} \right)$$

where f_p is a correction to the structural factor $S(Q)$; M is the averaged mass of scattering nuclei, $Q_0 = 2\pi/\lambda$ and E_0 is the energy of incident neutrons. According to Blech and Avenbach [22] the multiple scattering cross-section σ_m is

$$\sigma_m = \sigma_s \delta \frac{(\sigma_s/\sigma_t)}{1 + \delta(\sigma_s/\sigma_t)}$$

where σ_s is the scattering cross-section, σ_t is the total cross-section $\sigma_t = \sigma_s + \sigma_a$ where σ_a is the absorption cross-section and $\delta \sim 0.1$. According to the Debye equation, the RDF is the Fourier transformation of the normalized interference function $i(Q)$:

$$4\pi R^2 [\rho(R) - \rho_0] = \frac{2R}{\pi} \int_{Q_{\text{min}}}^{Q_{\text{max}}} Q i(Q) \times \sin(QR) M(Q) dQ$$

where ρ_0 is the average atomic density (at. nm⁻³) of the glass sample. The modified function $M(Q)$ is introduced to reduce the effect on the RDF of the limited value of Q_{max} .

The Fourier transformations of the normalized experimental curves $F(R)$ are shown in Fig. 2. The positions of the atomic density maxima observed on the RDF are listed in Table II. The RDFs in Fig. 3 are

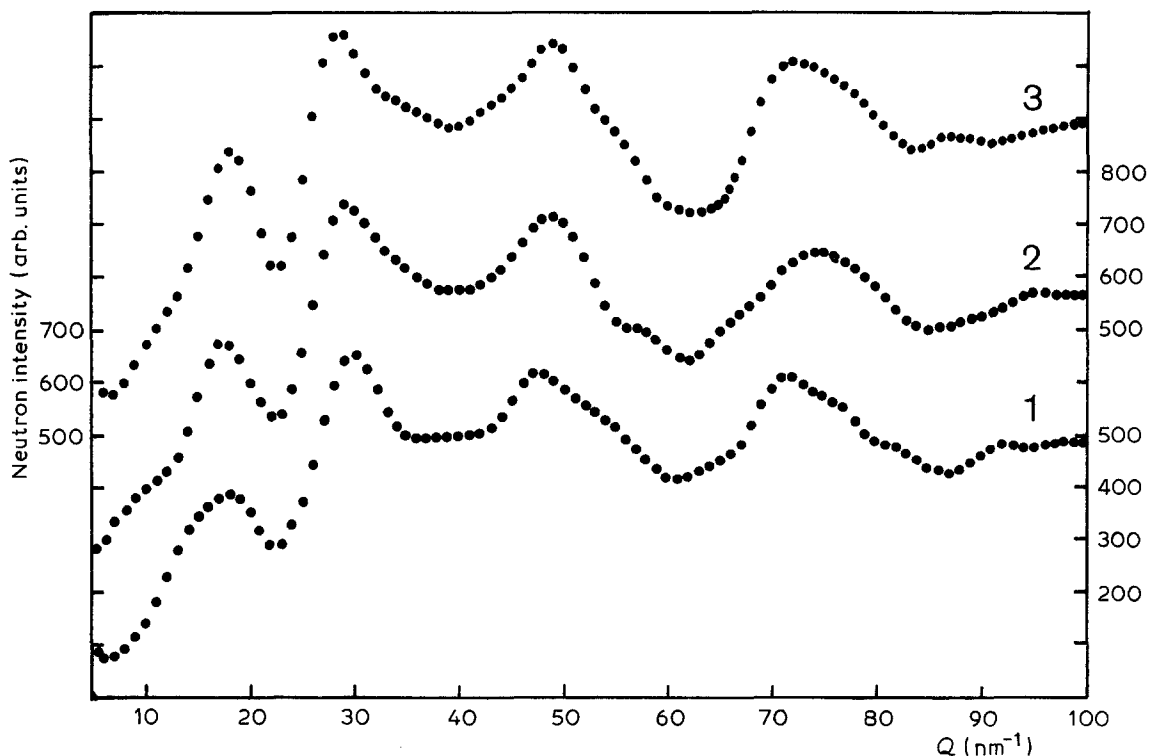


Figure 1 Experimental neutron interference functions $I(Q)$ for (1) TM1, (2) TM2 and (3) TM3 glass samples.

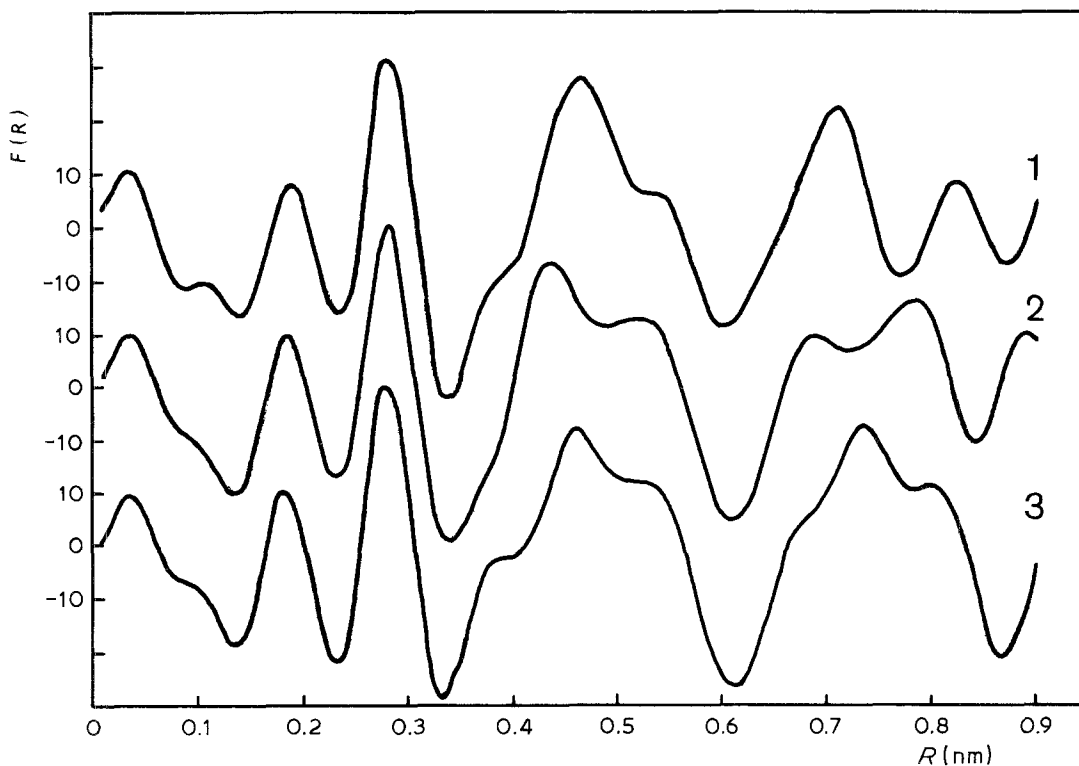


Figure 2 Fourier transformations of the normalized experimental data $i(Q)$ for (1) TM1, (2) TM2 and (3) TM3 glass samples.

calculated up to $R = 0.5$ nm, as we shall presently confine our discussion to distances within the first and second coordination spheres, which do not exceed 0.45 to 0.6 nm.

4. Discussion

The RDFs obtained for the $\text{MoO}_3\text{-TeO}_2$ system have all the features common to tellurite glasses. The P1

maximum reflecting the Te-O and Mo-O distributions is positioned at R values smaller than the average Te-O distances in $\alpha\text{-TeO}_2$. For samples TM2 and TM3, an essential influence on P1 is exerted by the distribution of Mo-O distances from the first coordination sphere, whose average value is smaller than the respective value for $\alpha\text{-TeO}_2$.

The stability in position and area of the P2 maximum,

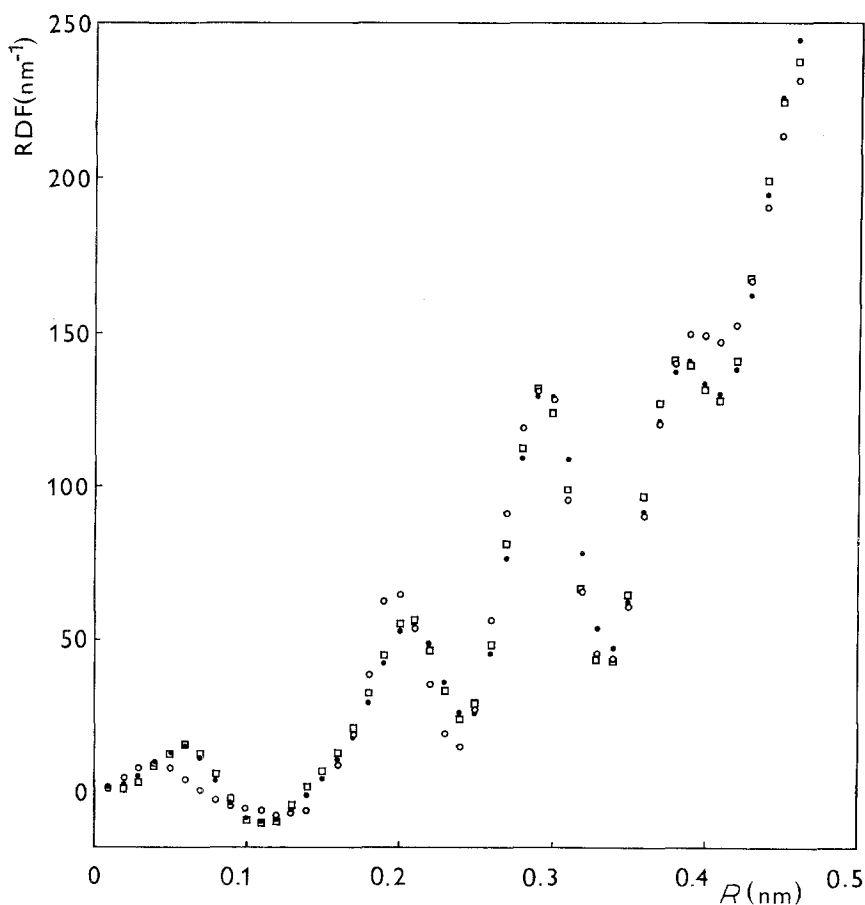


Figure 3 Total RDFs for (●) TM1, (□) TM2 and (○) TM3 compositions.

arising from the distribution of O–O distances, is relatively high. In the crystalline forms of α -TeO₂, MoO₃ and MoTe₂O₇ the shortest O–O distances have close values. This closeness must be expected to persist in the glassy TM1, TM2 and TM3 compositions. Experimentally a P2 peak is observed which is practically the same in spite of the considerable change in composition. The above-mentioned short-range order analogy between the crystalline and amorphous states is confirmed by a number of experiments, indicating that the basic structural formations are retained to a certain extent even in the liquid form. For instance, X-ray diffraction data for SiO₂ manifest the existence of SiO₄ tetrahedra in the temperature range from 293 to 1873 K.

The coordination maximum P3 at 0.39 to 0.4 nm (Fig. 3) is due to Te–(second O) and Te–Te interatomic distances. The experimentally observed reduction of its area relative to the model RDF for α -TeO₂ is another confirmation of the criterion for a glass transition in tellurite systems, as established by us [16–19]. The subsequent maxima P4 and P5 (Fig. 2) are at 0.475 and 0.55 nm, respectively, but their identification is hampered by the availability of a large number of interatomic distances in that range. The network in TeO₂-rich glasses is built up by bonding TeO₄ trigonal bipyramids by a common oxygen, correspondingly in axial-equatorial position relative to the tellurium atom. In this disposition the atoms occupy a small volume fraction within $0.13 \leq f \leq 0.30$ range [23]. For crystalline α -TeO₂ and MoO₃, f amounts to 0.28 and 0.30, respectively. The classification carried out [23] indicates that M_xO_y-type compounds form glasses if $f \leq 0.30$, that is, both oxides TeO₂ and MoO₃ are glass-formers.

The evolution of structure in the binary MoO₃–TeO₂ system has been investigated by Bart *et al.* [3]. The phase diagram exhibits a bertholide-type compound 2TeO₂ · MoO₃ (m.p. 824 K) and a marked tendency for glass-formation, because of its easy dissociation. This follows from the basic physical and chemical vitrification criteria. The X-ray diffraction study [3] of compositions containing MoO₃ below 33.3% reveals the simultaneous presence of α -TeO₂ and MoTe₂O₇ crystalline forms. For this reason one must take into account the influence of the MoTe₂O₇ structure in that concentration range (TM1). In this compound the tellurium atom is fourfold coordinated in relation to oxygen but in two different configurations (2 + 2) and (3 + 1) [4]. In both positions tellurium is in the Te⁴⁺ valence state. The alternative Te⁶⁺ state is not observed, since now the Te–O polyhedron must be in the form of a TeO₆ octahedron. The tellurium and molybdenum constant valence in MoTe₂O₇ relative to that in the starting TeO₂ and MoO₃ compounds shows that no significant change is to be expected in glasses from the MoO₃–TeO₂ system. The observed displacement of P1 towards the shorter values, relative to those existing in α -TeO₂ (Fig. 4), is due to the influence of the Mo–O distances. Four of them, with $R = 0.17, 0.174, 0.194$ and 0.195 nm, are shorter than the average value of the Te–O bonds from the first coordination sphere. The

TABLE III Quasi-crystalline model RDF

Sample	P1		P2	
	Position (nm)	Area (arb.u.)	Position (nm)	Area (arb.u.)
TM1	0.192 (0.202)	2.50 (2.48)	0.285 (0.284)	6.25
TM2	0.190 (0.195)	2.37 (2.40)	0.284 (0.285)	6.32
TM3	0.187 (0.195)	2.23 (2.43)	0.285 (0.282)	6.61

remaining two Mo–O distances are with $R = 0.214$ and 0.259 nm and exert no influence on the P1 peak position. Infrared spectroscopy investigations [13] reveal bands characteristic of α -TeO₂ and MoTe₂O₇ in TeO₂-rich glasses.

A value of 3.3 at $R = 0.192$ nm is obtained for the c.n. of the tellurium atom from the neutron diffraction data of TM1 glass. Considering the glass-formation process in tellurite glasses one should take into account the existing tendency towards lengthening [24] of one of the Te–O axial bonds. As a result, on increasing the content of the second component, tellurium is converted from fourfold to (3 + 1) coordination with respect to oxygen. Although in covalent bonded systems the angle changes mainly (up to 10%), while the bond lengths increase only slightly (within 5%), the lengthening of the (Te–O)_{axial} bond exceeds 10% in the glassy transition. This conclusion follows from the reduced area under P1 on the RDF of TM1 glass, as compared with the quasi-crystalline model RDF (Table III).

As the MoO₃ content is increased a marked increase is observed in the RDF of the short distances contributing to P1. There are no distances of that length in the paratellurite (α -TeO₂) [14]. In MoO₃ and MoTe₂O₇, where the irregular MoO₆ octahedron is the basic structural unit, the two shortest Mo–O distances are within the range 0.167 to 0.175 nm. The TM2 glass corresponds in composition to the MoTe₂O₇ compound. In crystalline samples of the MoO₃–TeO₂ system, the X-ray diffraction lines corresponding to α -TeO₂ disappear at 33.3% MoO₃. There is an alternative possibility for the formation of short-range order similar to a substitutional-type structure in the glassy state. However, this possibility is less likely here due to the following reasons [3]:

(i) The incorporation of MoO₆ units in the α -TeO₂ structure and vice versa will enhance the bonding by common edges and sides, which will in turn produce a strong electrostatic repulsion between the cations.

(ii) The crystalline structures of α -TeO₂ (tetragonal) and MoO₃ (orthorhombic) are too different from each other. Even in the MoTe₂O₇ structure the tellurium–oxygen and molybdenum–oxygen polyhedra are spatially differentiated into chains or layers, respectively.

In accordance with these considerations the interpretation of the RDF is carried out by comparing with model RDFs, which are constructed on the basis of α -TeO₂, MoO₃ and MoTe₂O₇ crystalline phases of different component ratios (Fig. 4). As is well known [6, 7], MoTe₂O₇ is easily fixed in a glassy state. From this it follows that in TM2 glass the short-range order is probably similar to the arrangement in the crystalline

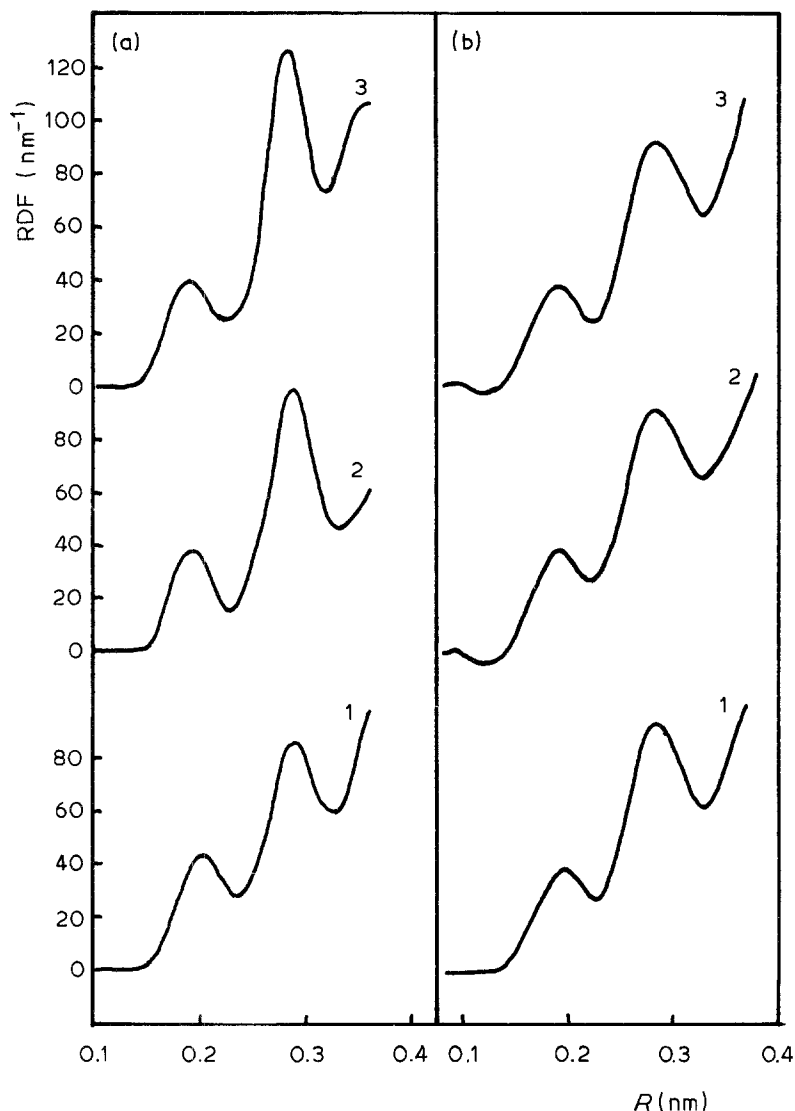


Figure 4 A comparison between (a) the quasi-crystalline RDFs (SD model) and (b) the experimental RDFs for (1) TM1, (2) TM2 and (3) TM3 glass samples.

state. The quasi-crystalline model RDF for MoTe_2O_7 (Fig. 4) coincides in general terms with the experimental RDF for the TM2 composition up to distances of 6.6 nm. There is a more substantial difference between the areas of the first coordination maxima. Because of the asymmetric disposition of the molybdenum atom in the MoO_6 octahedron, one of the Mo–O axial bonds is 0.25 nm long [3]. Its contribution will result in some displacement of the P2 peak towards shorter distances.

The Mo–O bond second in length is 0.214 nm and it falls in the minimum between P1 and P2. Therefore four Mo–O distances and the distribution of the lengths of Te–O bonds in TeO_4 bipyramids will both affect the P1 peak parameters. Our previous investigations [16–19] indicate that in tellurite glasses one of the $(\text{Te}-\text{O})_{\text{axial}}$ bonds undergoes lengthening above 0.22 nm. Here a definite tendency for a $\text{TeO}_4 \rightarrow \text{TeO}_{3+1} \rightarrow \text{TeO}_3$ transition is observed. Thus, as a result of the combined influence of the shorter Mo–O distances and of the more compact TeO_3 configuration, the P1 peak of RDF_{exp} shifts towards lower values of R . Bonding by a common edge, which joins the MoO_6 tetrahedra into double chains, is considerably stronger than the Mo–O–Mo bridging along the a axis. Consequently, a transition to MoO_5 coordination is probably due to the breaking of the long

Mo–O axial bond (0.26 nm), as the system goes into a disordered state.

The crystallisation products of TM3 glass are an admixture of MoTe_2O_7 and MoO_3 [3] in an approximate mole ratio of 1 : 1. Infrared spectra [13] confirm this fact; however, in the glassy state the band at 648 cm^{-1} shifts to 670 cm^{-1} because of the formation of TeO_3 groups. The short-distant P1 component of the RDF continues to grow. As a result its centre of gravity shifts to 0.187 nm, while its area decreases compared with the respective maximum of TM1 and TM2 compositions (cf. Table II). The reduction of the area S1 below the peak P1 cannot be solely explained with a tellurium atom change from fourfold to triple configuration. If in accordance with Dimitriev *et al.* [13] and Zeman [24] we assume that all tellurium atoms are surrounded by three oxygen atoms as nearest neighbours, the area S1 of the model RDF is about 15 to 20% larger than the experimental one. At the same time the total area S1 + S2 below P1 and P2 is hardly altered by the composition change. Such a fact can be explained by the changes taking place within the MoO_6 octahedron. The longest axial Mo–O bonds ($R = 0.26, 0.23 \text{ nm}$) in MoTe_2O_7 and MoO_3 , respectively, which are also the weakest ones, break down in the glassy state. The electric charge in the newly formed MoO_5 groups redistributes, as a subsequent transition

from the layer (MoO_3) to a chain configuration (MoO_4), is realized. As mentioned by Porai-Kozhiz and Atovmian [25] the stability of the $(\text{MoO}_4)^{2-}$ complex exceeds that of other ways of bonding. The bonding of MoO_4 tetrahedra into chains by means of a common oxygen, characteristic for molybdenum–oxygen compounds, probably exists in the investigated glasses as well. The distribution of Mo–O bond lengths in the deformed MoO_4 tetrahedron contributes to the P2 maximum of the RDF. This mechanism of structural build-up can explain the reduction of S1 simultaneously with the increase of S2.

As in other tellurite glasses [16–19], a weakly expressed maximum is observed in the range about 0.4 nm which exhibits a largely reduced height relative to the model quasi-crystalline RDF. In the crystalline structures of $\alpha\text{-TeO}_2$, MoO_3 and MoTe_2O_7 the coordination state of tellurium and molybdenum changes and there is a transition from three- to two- and one-dimensional formations. These occur as a result of the non-equilibrium glassy state. Particularly sensitive to the above transition are Te–Te cation distributions in the 0.4 nm range.

The changes in the short-range order in glasses from the $\text{MoO}_3\text{--TeO}_2$ system are close to those in the $\text{TeO}_2\text{--P}_2\text{O}_5$ system [16]. The combined influence of the two glass-formers affects mainly the structurally non-equivalent weak cation–anion and cation–cation bonds.

5. Conclusion

The results obtained in the present structural investigation, concerning the increase of MoO_3 content, can be generalized as follows:

1. The coordination state of the tellurium atom relative to the oxygen configuration changes from 4 to $(3 + 1)$ and 3.

2. Part of the MoO_6 octahedra pass into a new configuration, characterized by a reduced c.n. and MoO_4 formations are observed as well.

3. The oxygen network undergoes a weak deformation during the glassy transition and the average O–O distances remain practically unchanged.

4. The criterion for fixation in a glassy state of tellurite glasses, proposed by us earlier, is now confirmed; the coordination maximum at 0.4 nm is strongly reduced in $\text{MoO}_3\text{--TeO}_2$ glasses as well.

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