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Neutron diffraction investigation of a tellurite–tungstate glass*

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The short range atomic order of a 20 mol % WO_3–TeO_2 glass has been investigated. The alteration of the stereochemical polyhedra characteristics have been studied and correlation with the model $RDF_{partial}$ (radial distribution function) and RDF_{total} for TeO_2 and WO_3 glass has been carried out. A structural interpretation of the influence of the modifier on the P1, P2 and P3 peaks location has also been carried out. A comparison of $RDF_{partial}$ and RDF_{total} with RDF_{exp} curve of the glass has been accomplished. Stability of the O–O distances (peak P2) has been established as well as a broadening effect at Te–Te, Te–second O distances (peak P3). The Te–Te atomic distances are most sensitive towards glass transition. A structural model based on TeO_4, WO_4 and WO_6 polyhedra has been presented.

1. Introduction

Tellurite–tungstate glasses are classified as super heavy flint glasses. They exhibit a refraction index of $n > 2.0$ and a low dispersion value ($\nu \sim 18$). Optical properties of glasses have been defined in the investigations of Yakhkind [1], while glass formation regions have been determined by Imaoka [2, 3]. Reports on IR transmission of a glass with composition of 20 mol % WO_3 have been given [1, 4] (All concentrations are given in mol %.) Experimental data on glass formation region, properties, compositions and transmission visible and IR spectra have been reported for series of multi-component tellurite–tungstate glasses as well [5]. The authors use the TeO_2–WO_3 system as basic.

No data have been published on diffraction structural investigations of glasses in the TeO_2–WO_3 system. However, an IR spectroscopic investigation of glass with 5–45% WO_3 has been reported [6]. The authors are of the opinion that WO_3 does not lead to a tellurium coordination state change. For glasses with up to 30% WO_3 they suppose that part of the TeO_2 is replaced by WO_4 tetrahedra. A scheme of  $-\overset{|}{\underset{|}{Te}}-O-\overset{|}{\underset{|}{W}}-O-\overset{|}{\underset{|}{Te}}-$ bonding by substitution is presented. The model is valid for the TeO_2-rich glass region and is based on the observed intensive band at 925 to 935 cm^{-1}.

A determination of the glass properties in the binary system have been reported [7]. On the basis of IR spectroscopic investigation the author assumed that the glass network is built by both components, one from deformed TeO_6 octahedra and the other from WO_4 tetrahedra, which are incorporated in each other.

The results reported [8] show that in a $TeO_2 \cdot 23WO_3$ glass the WO_6 octahedra define the dielectric properties of the glass. A dipole–dipole interaction between the WO_6 octahedra defining the ferro-electric character of glasses in the range 12 to 23% WO_3 has been verified.

Braunstein and Lefkowitz [9] accept the existence of integration of WO_6 octahedra with a possible weak WO_6 deformation due to the glass-forming network. The author considers that not all of the WO_6 are equivalent. Photochromatic properties characteristic of such glasses are, mainly due to the double injection of electrons and ions.

This work presents a direct structure investigation for a glass with the composition 80% TeO_2 and 20% WO_3. The chosen composition is close to the eutectic point at 16.7% WO_3 [10]. This is a good base for a stable glass formation of the melt. Our goal has been to establish the modifier influence on the location of the peaks P1 and P2 on the RDF; to establish the influence on the tellurium atom coordination, on the Te–O matrix and expecially the influence on the Te–Te distances. We aimed to establish the influence of $RDF_{partial}$ on the total RDF_{exp} and RDF_{model} curves. The neutron diffraction method was chosen for the clarification of these problems because of its advantages in investigations of objects, which contain elements with considerably different atomic numbers

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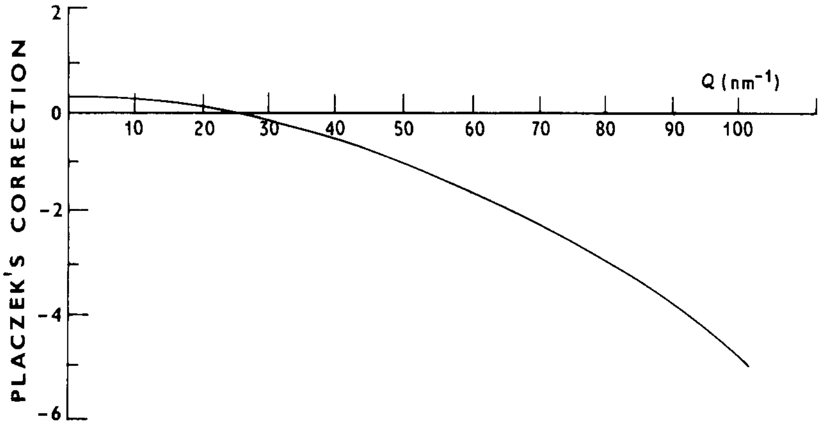

Figure 1 The dependence of Placzek correction on Q values for inelastic neutron scattering. $\lambda = 0.106\,\text{nm}$, $\bar{m} = \Sigma n_i m_i / N$.

Z, as is the case in the tellurium, oxygen and tungsten atoms. The coherent neutron scattering amplitudes are $0.545 \times 10^{-12}\,\text{cm}$ for tellurium, $0.580 \times 10^{-12}\,\text{cm}$ for oxygen and $0.48 \times 10^{-12}\,\text{cm}$ for tungsten atoms respectively. Therefore, the contribution of interatomic Te–Te, Te–O, W–O, O–O, etc. distances on the RDF will be of the same order.

2. Experiment and data processing

For structural investigations of glasses it is appropriate to make a correlation between a crystal structure and its glass analogue. This method is often the initial step for building up glass structure models. According to Yakhkind [10] no compound formation is observed up to 40% WO_3†. Moreover, the system is of a simple eutectic type with a minimum Δt value between the solidus and liquidus temperatures for composition over 16.7% WO_3. If a binary compound $TeWO_5$ (1 : 1) should be formed it would have a high dissociation ability. For this reason the method cited above cannot be applied in this case. In spite of this a composition with a 20% modifier is suitable since the tellurite melts are easily cooled in a vitreous state [5, 12, 13]. On the other hand the composition is appropriate for a comparison with our previous structural results for tellurite glasses [14–16].

The glass was synthesized from p.a. reagents TeO_2 and WO_3 (Merck) in 25 g quantities at a low pressure oxygen atmosphere according to the technology described earlier [5, 13]. In this method one may consider that in synthesis there are no reductive conditions, which may lead to a WO_3 non-stoichiometry and TeO_2 reduction. Thermally untreated sample was powdered and checked for amorphous structure by means of X-ray diffraction with a TUR M-62, Cu$K\alpha$.

Scattering curves of the powdered glass sample were taken by a neutron diffractometer DN-520 in the IRT 2000 reactor. Monochromatic beam with $\lambda = 0.1061\,\text{nm}$ was used, with a constant step of Q, $Q = 4\pi \sin \theta/\lambda$. A second neutron diffraction study has been made by TKSN 400 spectrometer in the Institute of Nuclear Physics, Řež at $\lambda = 0.101\,\text{nm}$. The maximal value of the scattering vector in both cases was $100\,\text{nm}^{-1}$.

RDF of atomic density was obtained by numerical integration of the Debye equation in the range $4-100\,\text{nm}^{-1}$:

$$4\pi R^2 [\varrho(R) - \varrho_0] = \frac{2R}{\pi} \int_{Q_{\min}}^{Q_{\max}} Qi(Q)M(Q) \times \sin QR \, dQ \qquad (1)$$

The authors used for a function-modifier $M(Q)$ the function given by Lorch [17]. The experimental spectrum values were corrected for inelastic scattering by the Placzek correction factor [18]. Its dependence on the scattering vector Q is shown on Fig. 1. The values of the multiple and incoherent scattering were defined by the least squares method where the oscillations on RDF at $R < 0.15\,\text{nm}$ were minimized. Besides the RDF_{exp} curves, on the basis of the $\text{RDF}_{\text{partial}}$ the $\text{RDF}_{\text{model}}$ curves were obtained by dissolving the initial crystal lattices by the method of structural diffusion [19] and subsequent summation in accordance with the molar concentration of the components.

3. Stereochemical characteristics of the polyhedra

Before a discussion of the atomic density RDF for the tellurite–tungstate glass it is useful to trace the stereochemical characteristics of the primary polyhedra used for the build-up of the vitreous network. The stereochemical characteristics will help in modelling the glass structure and it will be possible to compensate somewhat the impossibility of applying the method of structural correlation between the given crystal compound and its vitreous analogue in this case.

3.1. Coordination of the tellurium atom

The oxygen coordination around the Te (IV) is a trigonal bipyramid with one unoccupied position in the equatorial plane. Zemann and Pertlik [20, 21] postulate that the space location of the three oxygen atoms nearest to the Te atom is approximately the same, i.e. the dynamical change in the number of oxygen atoms leads to an alternation from 4th, through (3 + 1), to 3rd coordination. The averaged values of both the axial Te–O distances for many crystalline tellurites [22] are essentially different when compared with data for α-TeO_2 [23, 24]. This shows

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† Only the heteroacid $H_6Te(OWO_3)_6$ is known from literature [11]. It is formed by the bonding of the orthotellurite (Te^{6+}) acid oxygen ions with the respective acid anhydrides. In such a structure there are six WO_6 octahedra in a circle around the central TeO_6 octahedron and the bonding is edge by edge. This bonding impedes considerably the obtaining of tellurite–tungstate glasses.

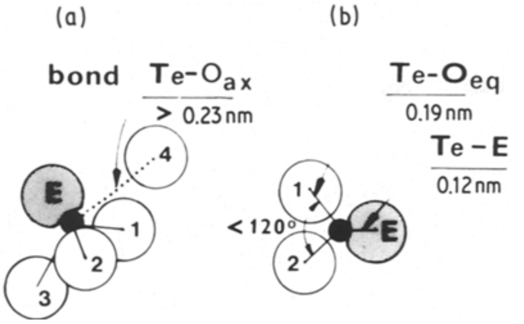
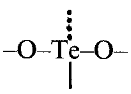


Figure 2 Stereochemical surroundings of the tellurium atom with elongation of one of the $-\overset{|}{\underset{|}{\mathrm{Te}}}-_{ax}\mathrm{O}-$ bond: (a) an illustration of the intermediate (3 + 1) type of coordination (TeO_4 polyhedron); and (b) a surroundings of the tellurium atom in the equatorial plane. E is a free electron pair. ○ is the oxygen atom, ● is the tellurium atom.

that the axial Te–O distances are not equivalent. The difference $\Delta\bar{R}_{3-4}$ is many times greater than that of $\Delta\bar{R}_{1-2}$ and $\Delta\bar{R}_{5-6}$ at Te–O bonding. Therefore, it is clear that one of the Te–O bonds in the TeO_4 polyhedron is strongly dynamic and it will be easily attacked by the modifier.

Naturally, not only the modifier polyhedra influence the stereochemical surrounding of the tellurium atom. There is also influence by the available free electron pair marked by E. This problem is considered in detail [25–27]. On the basis of generalization of contemporary crystallo-chemical knowledge on the oxygen surrounding of the tellurium atom, one could assume that the oxygen configuration exists as represented on Fig. 2. It is seen that E is situated in an unoccupied equatorial position. It tends to fill the free space around the tellurium atom to a maximum degree. This leads to a decrease in the values of the valence angles between the bond electron pairs. On the other side the polyhedra deformation will also depend considerably on the location of E.

Galy *et al.* [25] in parallel with the Gilespy's hypothesis [28] have proposed a hypothesis for the mechanism of the TeO_4 polyhedra deformation at the transition 4 → 3 + 1 → 3, in accordance with which the tellurium atom "rotates" in relation to E. This rotation is due to electrostatic repulsion forces between E and the neighbouring oxygen atoms. Because of this deformation, as it is seen from Fig. 2, the tellurium atom is not in the centre of the equatorial plane of the trigonal bipyramid. This follows also from the $Te–O_{eq}$ values with $R = 0.192$ nm, i.e. they are greater than the calculated Te–E value [25]. On the other side, at the most typical coordination satisfaction of the Te atom in tellurite glasses, i.e. (3 + 1) coordination satisfaction, it follows that the tellurium atom will be outside the equatorial plane because of the elongation of one of the $Te–O_{ax}$ bonds and the strong decrease in the angle



$$-\mathrm{O}-\overset{\vdots}{\underset{|}{\mathrm{Te}}}-\mathrm{O}-$$

On Fig. 3, $RDF_{partial}$ and RDF_{total} for a hypothetical TeO_2 glass calculated by the method of structural diffusion are presented in order to receive information for the 2nd and 3rd coordination sphere. Regardless of the unmarked maxima on the $RDP_{partial}$ curves, their contribution to the RDF_{total} curve may be clearly seen for a para-tellurite crystal network and for a TeO_2 glass, respectively. The contribution of 10 R_{Te-Te} distances, exhibiting chain–chain bonding is strongly manifested on the $RDF_{partial}$ of the α-TeO_2 curve at the distance 0.385 nm (the peak P3).

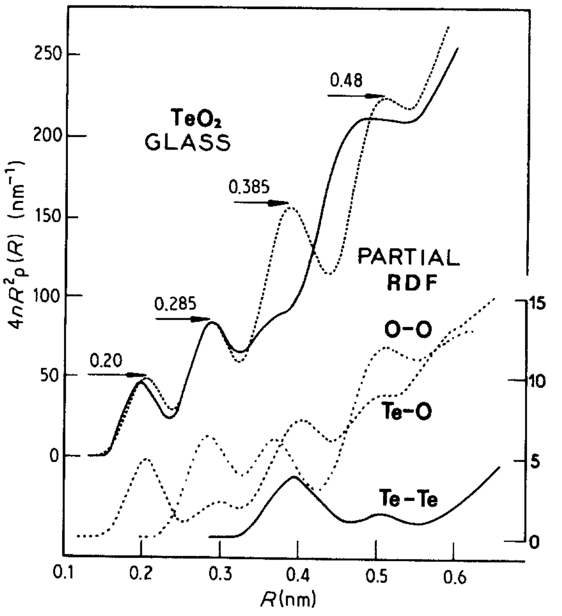


Figure 3 Comparison of the $RDF_{partial}$ and RDF_{model} for (· · ·) α-TeO_2 and for (——) a tellurite glass.

3.2. Tungsten–oxygen configuration

The structural chemistry of WO_3 is close to that of MoO_3. The detailed stereochemical investigation of these oxides and their compounds is given by Porai-Kozhiz and Atovmian [29]. As is seen from Fig. 4, the deformation of the WO_6 octahedra is weaker than that of MoO_6 octahedra, i.e. there is a pronounced tendency towards regular octahedral surrounding. It is known, however [29, 30], that all WO_3 modifications represent a deformed, although to different extents, three dimensional framework of WO_6 polyhedra bounded together by the "angular" oxygen. This occurs always with a long W–O bond situated in a trans-position (see Fig. 4 W–O (1) via W–O (6)) with

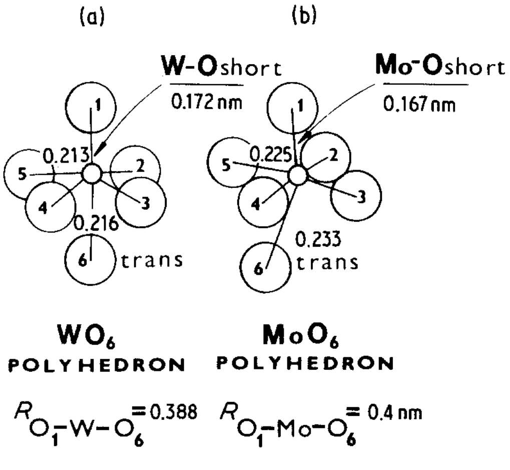


Figure 4 A juxtaposition of the parameter of (a) WO_6 and (b) MoO_6 polyhedron.

respect to the short W–O bond. The elongation of one of the W–O bonds in transposition gives reason to consider that tungsten atoms are slightly displaced from the centre of the WO_6 octahedra. This displacement is along the polar axis of the WO_6 octahedra and it leads to a contraction of one of the six W–O bonds and to an elongation of the opposite one (see Fig. 4a).

According to Ekström [31] there are tetrahedra, octrahedra and pentagonal bipyramids in the tungsten and molybenum oxides. The WO_6 octahedron is the base polyhedron. This one is bound with the surrounding polyhedra in four ways, only two of which are of interest for the structure formation of tungstate glasses, i.e.

(a) At bonding WO_6 has one or several not bridging oxygen atoms and

(b) The WO_6 octahedron inserts its oxygen atoms entirely in bonding vertex with vertex.

The former bonding is reported in the structure formation of some tungsten–phosphate glasses [32], the latter is assumed for crystals and glasses with high WO_3 concentration [33–35]. Because of the dynamic change in the Te–O bonds of the vitreous network, as is the case, there will be a relatively strong deformation of the W–O polyhedra as well. It would be expected that this deformation will occur at long W–O trans-bonds, which can be elongated to such a degree, that the tungsten atom may be really considered as four- or five-fold coordinated.

One can conclude from this discussion that the WO_6 polyhedra possess a lower degree of linear and angular deformation in comparison to MoO_6 octahedra. The shortest and strongest at the same time W–O bonds are situated in a cis-position with respect to one another. In the trans-position one can always find a proportionally elongated W–O bond, thus retaining a constant volume of the space reserved by the WO_6 polyhedra.

The following conclusions can be drawn from the analysis of $RDF_{partial}$ and RDF_{total} curves for a hypothetical WO_3 glass, presented on Fig. 5:

(a) the contribution of W–W distances to the RDF_{total} curve is small and can in fact be neglected;

(b) the $RDF_{partial}$ W–O curve is with three well-expressed maxima: P1 (0.190 nm) contribution from the distances in the WO_6 polyhedron; P2 (0.420 nm) contribution from the W–O distances of the second coordination sphere; and P3 (0.570 nm) distances of the third coordination sphere;

(c) the –O–O– distances have a contribution to the RDF_{total} curves, but only the first peak at 0.268 nm is well expressed.

It is seen from the RDF_{total} of the WO_3 glass that there is no expressed minimum between P1 and P2 around 0.225 nm. This shows that there is an instability in the unequivalent W–O bonds in the polyhedron. In essence, this is a weak displacement of the tungsten atom from the centre of the octahedron, whose asymmetry strongly depends on the manner of connection with the surrounding polyhedra. This deformation will be expressed more clearly when one or two of the oxygen atoms in the vertex are not bridged, which is typical in the formation of the vitreous matrix.

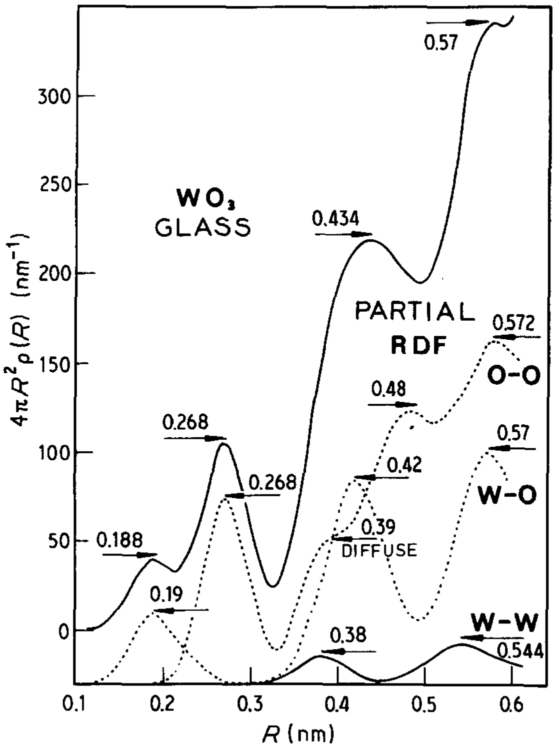


Figure 5 Comparison of $RDF_{partial}$ and RDF_{model} curves for a WO_3 glass.

4. Experimental results and discussion

From the directly measured diffraction spectrum, presented on Fig. 6 one can see that there exist four well-pronounced diffuse maxima. After a Fourier transformation of Equation 1 we obtain for $F(R)$:

$$F(R) = 4\pi R^2 [\varrho(R) - \varrho_0] \quad (2)$$

We have calculated the values of $F(R)$ for R up to 1.2 nm. Two $RDF_{partial}$ for the investigated glass are shown on Fig. 7. One of the curves is based on experimental data, and the RDF_{model} is calculated by the summation of the $RDF_{partial}$ for TeO_2 (Fig. 3) and WO_3 (Fig. 5) in the proportion 4 : 1. As is seen from Figs. 3 and 5, the peak P1 is a result of the radial distribution of Te–O and W–O distances of the basic polyhedra. At comparison of P1, three deviations from the model curve are outlined:

(a) a weak displacement of P1 towards the shorter distances

(b) a reduction of the height and area of the peak

(c) a weak displacement and lowering of the minimum between P1 and P2

This means that the atoms in the vitreous matrix are arranged so that their contribution does not define a strictly fixed local atomic configuration, i.e. there is a comparatively arbitrary distribution of –O–Te–O– and –O–W–O– angles and bond lengths. From the above said it can be assumed that the weak displacement of P1 is due to the influence of W–O building units and to the elongation of part of the $Te–O_{axial}$ or $W–O_{trans}$ bonds (overlapping of P1 and P2) with the

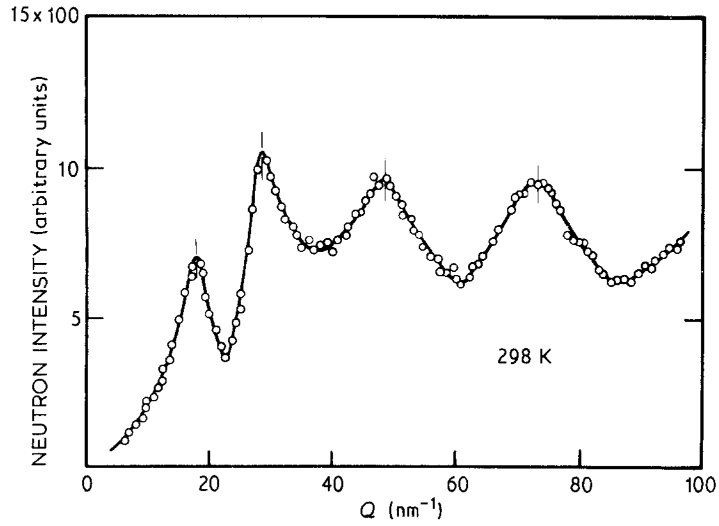


Figure 6 Neutron diffraction spectrum of the glass.

assumption that the TeO_4 polyhedron is more closely packed. This effect could not be explained in any other way but with the aspiration of E to occupy a symmetrical position around the tellurium atom at a comparativery low length variation of three of the four Te–O distances. Therefore, the coordination number of the Te atom is reduced. Perhaps, the modifier acts predominantly on the Te–O_{axial} bonding (direct information from RDF) and on E (indirect information from RDF).

On the other side, the close packing of the basic building units may be due to the lowering the coordination number for the tungsten atoms which at five-four-fold coordination would have a lower space occupancy in comparison with the WO_6 polyhedron. A partial isomorphic replacement of PO_4 tetrahedra by WO_4 polyhedra is assumed by Lagzdons *et al.* [32] for phosphate–tungstate glasses, by Deal *et al.* [36] for alkali borate–tungstate glasses and by Dimitrov *et al.* [6] for tellurite–tungstate glasses, at comparatively low WO_3 concentrations. For the structural packing of glasses, Coey and Murphy [37] have proposed a topological model and RDF for a 2064 atomic octahedral random network built up of AB_3 polyhedra with AB_6 octahedra bounded vertex to vertex. It has been established that the density is 11% higher than that of AB_3 (WO_3, AlF_3) structures.

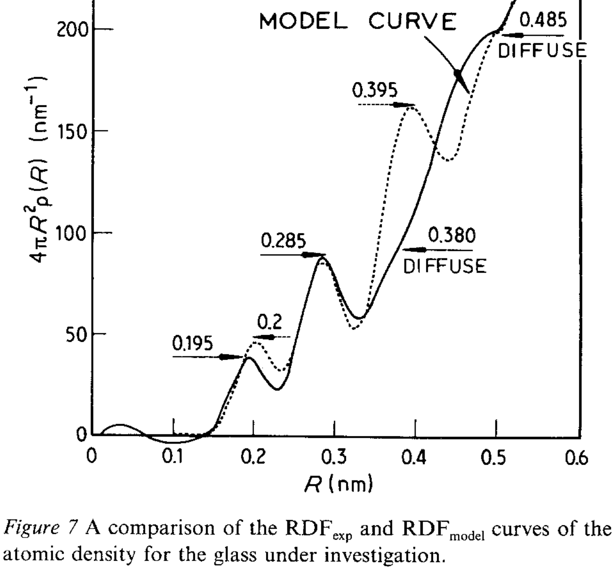


Figure 7 A comparison of the RDF_{exp} and RDF_{model} curves of the atomic density for the glass under investigation.

In order to clarify the problems we have carried out additional calculation for P1 and P2 and the data is represented on Table I. The results were obtained by approximation with Gaussian peaks by the least squares method. It is seen from the table that the area under P1 is decreased with 225 relative units due to a decrease in the coordination number. It is difficult to establish which of the coordination polyhedra gives a stronger contribution to P1. From Te–O partial RDF and from W–O partial RDF (Figs. 3 and 5) having maxima at 0.20 and 0.190 nm, respectively, it follows that the position of the maximum $P1_{exp}$ (0.195 nm) on Fig. 7 would have to be influenced mainly by the W–O surroundings. As an opposite tendency, however, this contribution may be strongly reduced in view of the TeO_2: WO_3 = 4 : 1 ratio in the glass.

From the RDF analysis one can establish that O–O distances in TeO_4 change insignificantly. There is polyhedra bonding vertex to vertex, the bonds of the type Te–O_{ax}–Te being preserved in the glasses with the simultaneous elongation of the Te–O_{ax} bonding and a comparatively weak deformation of the W–O polyhedra.

Having in mind the values $\chi_{Te} = 2.1$, $\chi_W = 2.0$ and $f_{Te} = 0.28$, $f_W = 0.24$, where χ is the electronegativity and f is the space occupancy, it becomes clear that both building units in the network have approximately the same χ and f. That is a good proposition for tetrahedral or octahedral participation of W–O polyhedra in the vitreous matrix.

The decrease of the maximum at P1 and of the minimum between P1 and P2 is predominantly due to the stronger influence of the W–O polyhedra on P1 and also to the deformation of the TeO_4 units at the glass transition. This shows that a fraction of the cation–oxygen distances elongate to about ~0.235 nm. This elongation however, is significantly smaller than for, e.g. glass with 20% P_2O_5 (see Fig. 8 and the data in Table II). The following conclusion can be drawn on comparing the two curves:

(a) There is a lower degree of secondary bonding and covalency in TeO_4 polyhedra;

TABLE I Characteristics of the peaks P1 and P2 from the RDF curves presented on Fig. 7

Peaks	P1		P2	
	RDF_{exp}	RDF_{model}	RDF_{exp}	RDF_{model}
Position (nm)	0.1949	0.1957	0.2850	0.2845
Half width ($\times 10^{-1}$ nm)	0.500*	0.506	0.700	0.691
Area (mm^2)	775	1000*	–	–
Intensity (arbitrary units)	3849	4493	8899	8496

*Fixed parameter.

(b) The Te–O_{ax} bond of the TeO_4 building unit is not so dynamic as is the case when the second glass former is P_2O_5 or B_2O_3. Thus, the tendency to secondary bonding by elongation of the four-fold Te–O bond above 0.24 nm, is not manifested here so well;

(c) Approximately 1/5 of the Te–O and W–O bonds change on account of the elongation of a fraction of the labile bonds; the others undoubtedly are shortened (interpretation from the position of P1).

Comparing the oxygen P2 peak on Figs. 3, 5 and 7 one can establish that it is significantly more stable than P1 and P3. This shows that the O–O distances in the polyhedra are the most stable, and the 6 O–O distances at the bonding of TeO_4 polyhedra have a dominating influence on the position of P2 at 0.285 nm. On comparing this peak with the position of P2 given by Neov *et al* [15, 16, 38] it becomes clear that it is stable for the glass under investigation, also.

The theoretically well-defined P3 peak, which is due to the contribution of 10 Te–Te, 2 O–O, W–W and O–O distances (see RDF on Figs. 3 and 5) is not recorded on RDF_{exp}. This peak is strongly "diffusive" (a "smearing" effect) and it confirms the results of our previous structural investigations [14, 16, 38]. Our interpretation of this region of atomic arrangement in the glass is that there is strong deformation of the bonds contributing to the RDF around 0.38–0.39 nm. The analysis shows that the modifier polyhedra are incorporated between the glass-former chains as well as into them. The latter is easily feasible in view of the same space occupancy of tellurium and tungsten atoms in Te–O and W–O polyhedra. It may be seen from the curves on Fig. 8 that every subsequent atomic distribution will not have a clearly expressed contribution to RDF_{exp}, due to the increase in the atomic density for values above 0.32 nm. It might be assumed that this structural deformation of the bonds is due to the incorporation of the modifier polyhedra in the tetrahedral voids of the para-tellurite structure and to the variation of the angle $-\underset{|}{\overset{|}{Te}}-_{eq}O_{ax}-\underset{|}{\overset{|}{Te}}-$ at simultaneous elongation of the –Te–Te– and Te–second O bonds, provoked by this incorporation.

The structural model illustrated on Fig. 9 might be assumed as highly probable on the basis of the discussion of a glass near to the eutectic point in this system. The model is based on the assumption that the glass formation in the tellurite system is characterized by:

(a) incorporation of the modifier polyhedra in the Te–O chains as well as between them;

(b) a local deformation of some of the bonds, angles between them and disruption of the chains and the respective layers in some places;

(c) the weak metal–metal "bonds" undergo deformation by elongation of distances, with a fraction of modifier polyhedra incorporating into the tetrahedral voids between the Te–O chains.

It is also valid for the glass under investigation that:

(d) the layers are connected by bridging oxygen ($-\underset{|}{\overset{|}{Te}}-O-\underset{|}{\overset{|}{Te}}-$, $-\underset{|}{\overset{|}{Te}}-O-\underset{|}{\overset{|}{W}}-O-$ or $-Te-O-\underset{/\,\backslash}{\overset{\backslash\,/}{W}}-O-$) or by the modifier polyhedra;

(e) a number of W–O polyhedra occupy a site position through incorporation into the tellurite chains and layers;

(f) in the case there are two ways of bonding tungsten ions, i.e. tungsten atoms in (IV) and (VI) coordination, incorporated into the chains as well as into the layers between them;

(g) W(VI) atoms have an underlined tendency to preserve their initial octahedral surrounding (see Figs. 4 and 5).

5. Conclusion

The following conclusions can be drawn on the basis

TABLE II Interatomic distances composition of the first five peaks for the tellurite glasses under investigation

Glass composition	Interatomic distances (nm)					Coordination number Tellurium	Reference
	$\bar{R}_{Te-O}$	$\bar{R}_{O-O}$	$\bar{R}_{Te-Te}$	$\bar{R}_{O-O}$	$\bar{R}_{O-O}$		
α-TeO_2 (crystal)	0.20	0.297	0.387	0.478	0.563	4	p.w.*
TeO_2 glass (theoretical)	0.20	0.285	0.385	0.480	0.645	4	p.w.
TeO_2 (80%) WO_3 (20%)	0.195	0.285	0.380(d)†	0.485(d)†	–	<4	p.w.
TeO_2 (80%) Li_2O (20%)	0.193	0.290	0.395(d)†	0.487(d)†	0.560	<4	[15]
TeO_2 (80%) P_2O_5 (20%)	0.180	0.275	0.39(d)†	0.475	0.55(d)†	<4	[16]
WO_3 glass (theoretical)	0.188	0.268	–	0.434	0.57	–	p.w.
Peaks	P1	P2	P3	P4	P5		

*Present work.
†A "diffusive" peak.

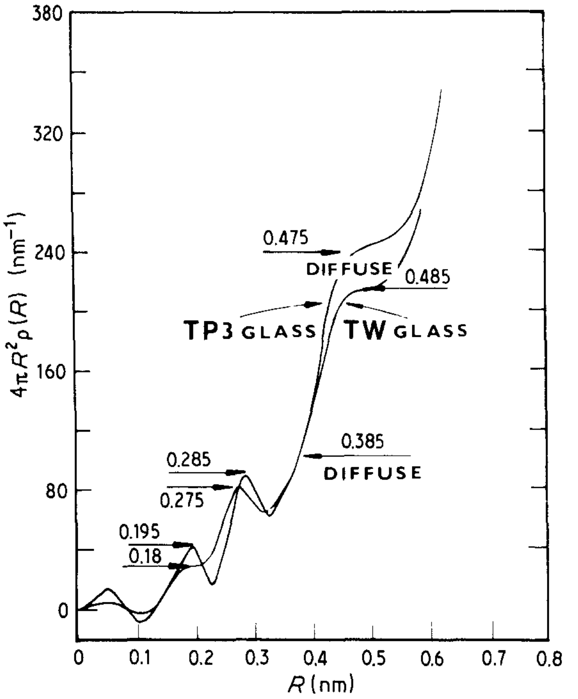


Figure 8 A correlation of the position and the change in the peaks P1 and P2 in accordance with the RDF_{exp} for the glasses with composition TP3 (80% TeO_2, 20% P_2O_5) and TW (80% TeO_2, 20% WO_3).

of the experiments and the analysis of the RDF curves:

1. The stereochemical configuration of Te–O polyhedra in the tellurite glasses does not have a strictly fixed geometry (see Table II).

2. An area reduction of the P1 peak was established, i.e. the reduction of the coordination number of the tellurium atoms. This leads to a densification of the TeO_4 polyhedra as a result of the equivalency of the three (two equatorial and one axial) Te–O bonds in the basic structural unit which make up the glass matrix.

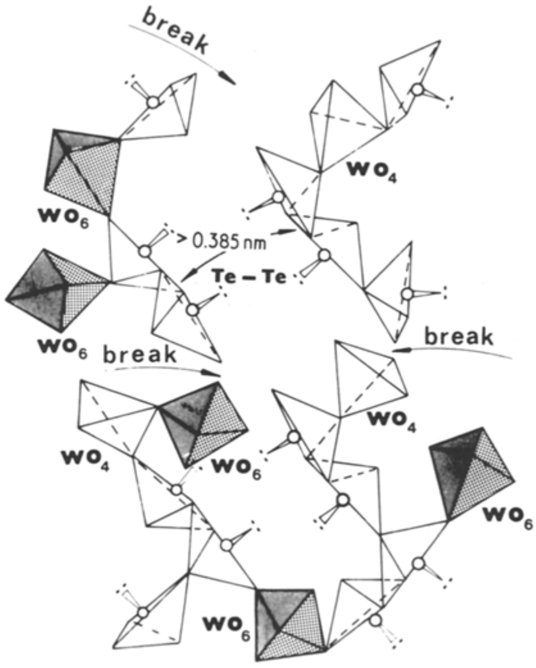
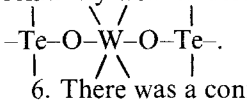


Figure 9 A model illustrating the manner of bonding of the nearest coordination polyhedra in the glass.

3. It was established that one of the $-\mathrm{Te}-_{ax}\mathrm{O}-$ bonds undergoes elongation, the $-\mathrm{O}-\mathrm{Te}-\mathrm{O}-$ angle deforms and because of the "open" structure of the TeO_4 polyhedron and its lower stability, the tellurite–oxygen network deforms at the vitrification.

4. The authors' concept that the modifier exerts the strongest influence on the distances above 0.335 nm.

5. It was shown that the –O–O– distances of the first coordination sphere remain unchanged. The TeO_4 polyhedron preserves its surroundings of four oxygen atoms since one Te–O bond elongates with about 20%, i.e. there is (3 + 1) coordination state of tellurium atom. WO_6 polyhedra undergo a relatively weaker deformation at bonding of the type



$-\mathrm{Te}-\mathrm{O}-\mathrm{W}-\mathrm{O}-\mathrm{Te}-$.

6. There was a confirmation that the $-\mathrm{Te}-\cdots-\mathrm{Te}-$ atomic distances around 0.385 nm are the most sensitive to the glass transition. This "smearing" effect on RDF can be assumed as due to the modifier incorporation (predominantly WO_6 polyhedra) into the voids along the "C" axis for α-TeO_2 in the strongly covalent and "open" three-dimensional tellurite matrix. Considerable freedom of rotation and a change in the $-\mathrm{Te}-_{ax}\mathrm{O}_{eq}-\mathrm{Te}-$ angle is assumed for TeO_4 polyhedron.

7. The structure of this glass can be described as a highly covalent "open" layer structure, which easily deforms at the modifier incorporation. The energy for transition to the glassy state is exclusively low at this manner of bonding and tellurite matrix deformation.

References

1. A. YAKHKIND, *J. Amer. Ceram. Soc.* **49** (1966) 670.
2. M. IMAOKA, "Advances in Glass Technology" Technical Paper 6th International Congress on Glass, Washington D.C., July 1962 (Plenum Press, New York) p. 149.
3. M. IMAOKA and T. YAMAZAKI, *J. Ceram. Soc. Jpn* **76** (1968) 160.
4. V. ZLOMANOV, O. TANANAEVA and A. NOVOSELOVA, *Zh. Neorg. Khim.* **5** ((1960) 1639.
5. V. KOZHUKHAROV, M. MARINOV and I. GUGOV, *Glastechn. Ber. Sonderband LVIK*, Proceedings of XIII International Congress on Glass, Hamburg, 4–9 July 1983, Vol. **56K** (Deutschen Glastechnischen Gesellschaft, Frankfurt, 1983) p. 839.
6. V. DIMITROV, M. ARNAUDOV and Y. DIMITRIEV, *Monatshefte Chem.* **115** (1984) 987.
7. Z. ZENG, *J. Chin. Silic. Soc.* **9** (1981) 228.
8. R. BRAUNSTEIN, *Solid State Commun.* **28** (1978) 843.
9. R. BRAUNSTEIN and I. LEFKOWITZ, *Ferroelectrics* **27** (1980) 225.
10. A. YAKHKIND, "Structura i Fizikokhimicheskie Svoistva Neorganitcheskich Stekol" (Khimia, Leningrad, 1974) p. 300.
11. H. EVANS, *J. Amer. Chem. Soc.* **70** (1948) 1291.
12. V. KOZHUKHAROV, M. MARINOV and G. GRIGOROVA, *J. Non-Cryst. Solids* **28** (1978) 429.
13. V. KOZHUKHAROV, M. MARINOV, I. GUGOV, H. BÜRGER and W. VOGEL, *J. Mater. Sci.* **18** (1983) 1557.
14. S. NEOV, I. GERASIMOVA, K. KREZHOV, B. SIDZHIMOV and V. KOZHUKHAROV, *Phys. Status Solidi (a)* **47** (1978) 743.
15. *Idem, J. Phys. (C) Solid State* **12** (1979) 2475.
16. S. NEOV, I. GERASIMOVA, V. KOZHUKHAROV and M. MARINOV, *J. Mater. Sci.* **15** (1980) 1153.
17. E. LORCH, *J. Phys. (C)* **9** (1969) 229.

18. G. PLACZEK, *Phys. Rev.* **86** (1952) 377.
19. G. PRINS, *Naturwissenschaft* **19** (1931) 435.
20. J. ZEMANN, *Monatshefte Chem.* **102** (1971) 1209.
21. F. PERTLIK and J. ZEMANN, *Öster. Acad. Wiss. Mater. Naturwiss.* **Kl**. Anz. (1971) 175.
22. M. TRÖMEL, private communication (1978).
23. J. LECIEWICZ, *Zh. Kristall.* **116** (1961) 345.
24. O. LINDQVIST, *Acta Chem. Scand.* **22** (1968) 977.
25. J. GALY, G. MEUNIER and S. ANDERSON, *J. Solid State Chem.* **13** (1975) 142.
26. I. BRAUN, *ibid.* **11** (1974) 214.
27. G. BAYER, *Fortschr. Mineral.* **46** (1969) 42.
28. R. GILESPY, *Geometria molekule* (Mir, Moskva, 1975) p. 98.
29. M. PORAI-KOZHIZ and L. ATOVMIAN, "Kristallokhimia i Stereokhimia Koordinazionnikh Soedinenii Molibdena (Nauka, Moskva, 1974) p. 6.
30. A. WELLS, "Structural Inorganic Chemistry" Fourth Edn. (Pergamon Press, Oxford, 1975) p. 289.
31. T. EKSTRÖM, *Chem. Commun. Univ. Stockholm* **7** (1975) 57.
32. J. LAGZDONS, Y. KLEPERIS and A. LUSIS, *Fiz. Khim. Stekla* **5** (1979) 141.
33. Y. MIROSHNICHENKO and V. MOMBELLI, *ibid.* **5** (1979) 30.
34. M. IMAOKA and H. NASEGAWA, *Yogyo-Kyokai-Shi.* **84** (1976) 390.
35. H. NASEGAWA and M. IMAOKA, *ibid.* **88** (1980) 122.
36. D. DEAL, M. BURD and R. BRAUNSTEIN, *J. Non-Cryst. Solids* **54** (1983) 207.
37. J. COEY and P. MURPHY, *J. Non-Cryst. Solids* **50** (1982) 125.
38. V. KOZHUKHAROV, H. BÜRGER, S. NEOV and B. SIDZHIMOV, *Polyhedron* in press.

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