STRUCTURAL STUDIES OF GLASSES BY TRANSMISSION ELECTRON MICROSCOPY AND ELECTRON DIFFRACTION

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Structural studies of glasses are a important part of materials science. The modern concepts for the glass structure are based on the idea of several structural levels in the amorphous solids: short range order (SRO), intermediate or medium range order (IRO) and local atomic imperfections. The SRO is characterised by the bonds lengths of the atoms in the first co-ordination shell, the bond angles, the co-ordination numbers and the type of corresponding polyhedron. The IRO is determined by the relative orientation of adjacent units (connection mode, bond angle and bond torsion angle) and by the network topology (topological cluster type and ring statistics). Structural peculiarity of the multicomponent glass are different inhomegeneities due to liquid-liquid phase separation.

The modern structurally sensitive methods in glass science -diffraction, spectroscopic and electron probe analysis, answer the question about the existence and evolution of one or of several structural levels. The transmission electron microscopy (TEM) as a part of the electron probe methods is applied for studying different types of microheterogeneities and nano-scale clusters in glasses. The first applications of TEM for the glass structure studies are related with the characterisation of different types heterogeneities [1-4] and the immiscibility in glasses [5-8].

The electron diffraction (ED) is suggested simultaneously as electron probe and diffraction method and gives data about the main structural units and the geometry of the SRO in glasses. The theory of radiation scattering (X-ray, neutron or electron) by amorphous solids is discussed by many authors [9-22].

The purpose of this work is to present information about the application of TEM and ED for structural investigations of glasses at different hierarchical levels using our experience in this field [23-38].

Our TEM investigations are carried out on some binary and on a large number ternary borate-tellurite systems where glass-forming oxides, oxides of transitional elements and modified oxides of elements from I, II and III groups in the Periodic Table, are used as third components. The accumulation of abundance of structural data from TEM observation (using transmission electron microscope EM-301, Philips, with C+Pt replica technique) of microheterogeneities, allows to make their classification and that could be spread out the structure peculiarities in other glass-forming systems. According to their origin the microheterogeneous structures in glasses were classified as follows: -

heterogeneities due to metastable immiscibility, presented morphologically as droplet-like formations (binodal decomposition), interpenetrating microphases (spinodal decomposition), mixed microstructures and complex micro-aggregates; - heterogeneities due to technological reasons; - microstructures revealing the correlation between the phase separation and crystallisation processes.

The heterogeneities related to metastable immiscibility were observed in many binary and ternary glasses. The low viscosity of the TeO_2 based glasses allows the liquid phase separation development during the cooling of the melts. *Fig.1* (a-d) illustrates the mentioned types of liquid phase separation structures.

One special case of microheterogeneities with technological origin occurs near the boundary between the two immiscible liquids obtained at macro-phase separation. Thus as a result of unfinished state of this process, during the cooling, drops from each melt stay in the other one. As the melting is not yet technologically complete, the drops cannot reach and infuse in their own melt This kind microimmiscibility formations were observed in glasses of the system TeO_2-B_2O_3-SiO_2 because of the high viscosity of the melts containing both B_2O_3 and SiO_2 glass-formers [3].

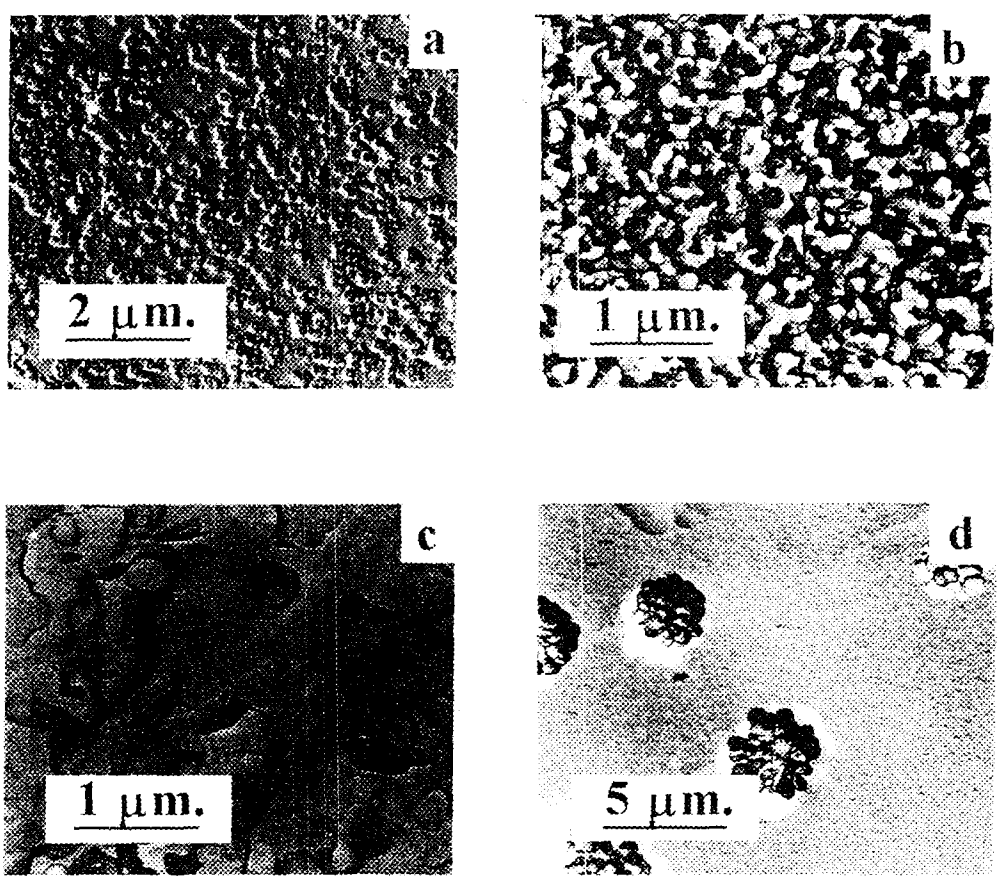

Figure 1: Metastable immiscibility microstructures with different morphology: a) droplet-like formations in glass with composition $70TeO_2,20B_2O_3,10Al_2O_3$; b) interpenetrating microphases in glass with composition $50TeO_2,50GeO_2$; c) mixed microstructures between droplet-like and interpenetrating phases in glass with composition $30TeO_2,30B_2O_3,40GeO_2$; d) complex micro-aggregates in glass with composition $95TeO_2,5B_2O_3$.

The correlations between the phase separation and crystallisation lead to formation of various heterogeneities in glasses. Following the scheme, proposed in [39] the main types of relationships between the two processes are: i) crystallised immiscibility drops - nuclei for matrix crystallisation; ii) drops crystallisation in amorphous matrix or amorphous drops in crystallised matrix; iii) independent crystallisation of both matrix and droplet-like phases. Microstructures due to these correlation are presented in [28].

TEM was used also for direct observation of the glass structure. We studied the nano-scale structure of borate glasses obtained at slow and fast cooling of the melts. After « in situ » heating with the electron beam in the electron microscope column, the development of structure in quenched glass is observed. The explanation of the cluster formations in borate matrix is made by computer simulation experiments [26].

The electron scattering application in glasses is not so popular as the X-ray and neutron diffraction. In the same time the ED possesses advantages for analysis of amorphous thin films or microparticles and it is very useful technique for SRO study in materials containing simultaneously light and heavy elements. Table 1 presents a comparison between the possibilities of the three diffraction techniques.

The theory of neutron, X-ray and electron diffraction by amorphous solids is one and the same. The intensity scattered by a non-crystalline solid is presented as a function of scattering vector S for elastic scattering. The neutron, X-ray or electron wavelength, λ, is unchanged on scattering and the magnitude of $S = 4\pi \sin\theta/\lambda$.

The intensity curve I(S) is the direct experimental result of the diffraction investigation. The Furrier transformation (FT) allows the transformation of I(S) in radial distribution function (RDF) of atoms. The RDF gives information on the amorphous material structure as follows:

- the positions of the maxima determine the interatomic distances in the different co-ordination shells;

- the areas under the maxima determine the co-ordination number for different co-ordination shells;

- the changes of the angles between different peaks compare the bond lengths in the amorphous and crystal material.

Table 1.

Parameters	X-ray diffraction	Neutron diffraction	Electron diffraction
Wave length λ, [nm]	0.05-0,25	0.01-2	0.0038 (at 100 kV)
S_{max} , [nm^{-1}]	~1,00	~0,60	~1,60
Atomic factor	~10^{-11} cm	~10^{-12} cm	~10^{-8} cm
Thickness of sample	bulk samples	bulk samples	microvolumes, thin films
S dependence	depending on S atomic factor	isotropic atomic factor	depending on S atomic factor
Magnetic scattering	no	additional scattering, depending on S	no
Detection	a)photographic films b)proportional counters c)scintillation counters	a)$^{10}BF_3$ or ^3He proportional counters b) ^6Li scintillation counters	a)photographic plates b) scanning devices
Advantages	a)easy production b)location of heavy atoms c)sample size > 1mm	a)location of light atoms b)distinguishing of atoms of neighbouring atomic number c)bulk samples (1-2cm)	a) study of thins films and microvolumes b)simultaneous location of light and heavy atoms
Problems	a)no simultaneous location of light and heavy atoms b)multiple scattering	a)multiple scattering b)magnetic scattering c)difficult production	a)inelastic scattering b)multiple scattering

Before the calculation of the RDF several corrections of the I(S), different for the three methods, should be made. In the case of ED, a correction for incoherent scattering is very important. There are several methods for background determination. We used the method of Tatarinova [9] and for the vitreous TeO_2 - the method of comparison with the background of the corresponding crystal modification [40]. Normalisation of the coherent part of the experimentally obtained intensity curve in respect to the curves of the independent atom scattering of the electrons is also made. Corrections for incoherent scattering could be very successfully made by energy-filtered electron diffraction (EFED) technique [41].

Our ED investigations of the SRO began with vitreous SiO_2. The SiO_2 was chosen as a test for the validity of the technique applied because of the SRO data abundance, obtained by X-ray, neutron and electron scattering. As it could be seen from Table 2, our results are compatible with the data of other authors.

Table 2

Author	Form	S_{max} ($Å^{-1}$)	Radiation	r_{Si-O} (Å)	r_{O-O} (Å)	r_{Si-Si} (Å)	n_{Si-O}	Si-O-Si
Coleman, 1967	film	16	e^-	1.62	2.65	3.05	4	145°
Pavlov, 1967	film	6.5	e^-	1.60	2.65	3.10	3.9-4.2	-
Nagasima 1970	film	11.5	e^-	1.62	2.60	3.10	4.1	147°
Nagasima 1972	film	12.5	e^-	1.62	2.60	3.05	4.1	147°
Mozzi & Warren, 1969	glass	20	x	1.62	2.65	3.12	3.77	144°
Gokularat-hnam, 1972	glass	14	x	1.65	-	-	-	-
Loshma-nov, 1974	glass	13.5	n	1.63	2.65	3.20	-	-
Gould, 1974	glass	8	x	1.64	-	3.10	-	-
Qin & Hobbs, 1995	glass	16	e^-	1.60	2.60	-	~4	150°
Grimley, 1990	glass	45.2	n	1.608	2.626	3.077	3.85	144°
Our results	glass film gel 200° 600°	18	e^-	1.63 1.60 1.60 1.62 1.63	2.61 2.60 2.60 2.60 2.60	3.16 3.15 3.15 3.16 3.18	4.1 3.9 3.9 3.6 4.1	150°

The ED study of the SRO was continued on vitreous B_2O_3 and TeO_2 and also on binary and ternary glasses with participation of these glass-formers obtained as bulk samples or thin films by traditional melting or by sol-gel technology *(Table 3)*. Figures 2 and 3 show the RDFs of some glasses investigated.

Table 3

Sample	r_{Te-O} (Å)	r_{O-O} (Å)	r_{Te-Te} (Å)
TeO_2	1.90	2.91	3.62
TeO_2	1.92	2.90	3.61

Sample	r_1 (Å)	r_2 (Å)	r_3 (Å)	r_4 (Å)
$80TeO_2$. $20B_2O_3$	1.92	2.55	3.63	-
$4TeO_2$. $96B_2O_3$	1.38	2.22	2.92	3.60

The comparison of the SRO data for vitreous SiO_2 with the results of other authors confirm the validity of the technique applied. It is established that the method of synthesis influences the SRO parameters. The decrease of the Si-O distances in SiO_2 films could be assigned to an additional deformation of the SiO_4 tetrahedron. The ED investigations of the SiO_2 gels showed that after thermal treatment at 600°C their structure is close to the structure of glass obtained by traditional melting. At the same temperature for B_2O_3-SiO_2 gels the transformation of the fourfold siloxane rings in sixfold rings is found.

The RDF obtained by ED of vitreous B_2O_3 and TeO_2 gave information about the main structural units building their glassy networks. The formation of B_2O_6 rings together with BO_3 groups in the borate network is confirmed. It is proved that TeO_4 groups are the main structural units in the network of the vitreous TeO_2 and its SRO is similar to that one of α-TeO_2. The RDFs of glasses of the system TeO_2-B_2O_3 are influenced mainly by B-O and Te-O distances. The predominating polyhedra in the topological network of B_2O_3-SiO_2 glasses vary with the composition. One possibility for application of ED for SRO investigations of multicomponent system is shown by TeO_2-B_2O_3-SiO_2 glasses *(Fig.3)*. Their structure comprise independent polyhedra participating simultaneously in one and the same network.

The examples presented illustrate some application of TEM and ED for structural studies of glasses. The information obtained concerns different structural levels and should be completed with the results obtained by other structurally sensitive methods.

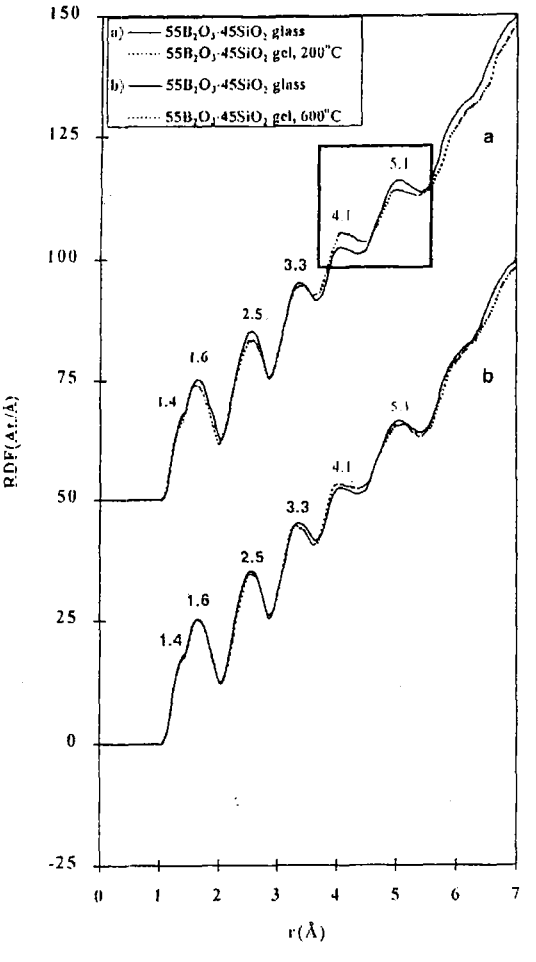

Figure 2: RDF of $55B_2O_3$.$45SiO_2$ glass and gel, thermaly treated at 200°C and 600°C

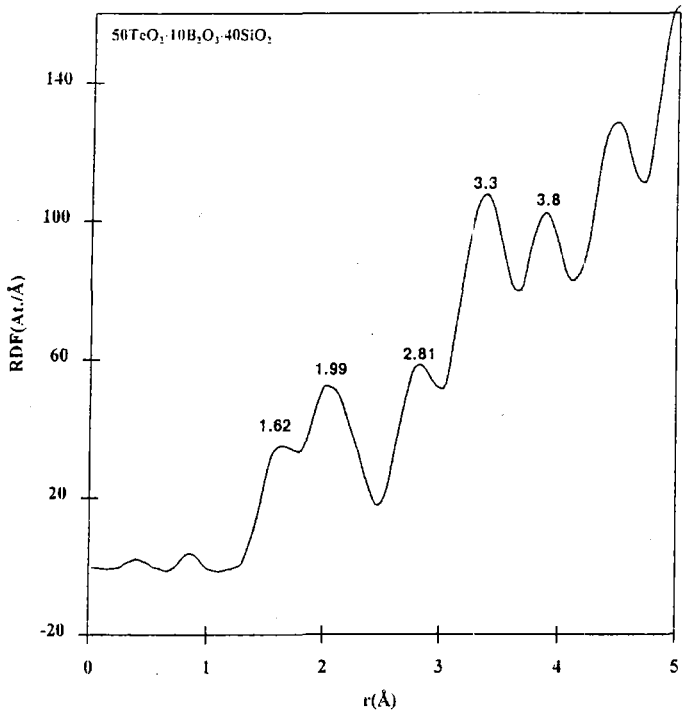

Figure 3: RDF of $50TeO_2.10B_2O_3.40SiO_2$ glass

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