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Phase equilibrium, glass-forming, properties and structure of glasses in the TeO_2–B_2O_3 system

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Phase equilibrium, glass-forming, properties and structure of the glasses in the TeO_2–B_2O_3 system have been investigated. The phase diagram is a simple eutectic-like type without any compound formation. A wide region of stable phase separation has been established. A monotectic temperature at 934 K and nonvariant point at 73.6% TeO_2 has been determined. The temperature dependence of the stable phase separation in the system has been studied. Some properties (density, transformation temperature, softening point, coefficient of thermal expansion, hardness, absorption in the UV and VIS region) of the tellurite borate glasses have been investigated. A structural interpretation of the glasses, on the basis of B^{11} NMR spectra was undertaken and two coordination states of boron atoms have been established. A simple model of two tellurium–boron–oxygen building units is presented.

1. Introduction

Glasses with TeO_2 as a glass-former have been studied more intensely recently. The most extensive works on the subject in relation to the investigation of the glass-formation range (GFR) [1–4], and properties of the glasses [3–6], show that the tellurite glasses are new optical materials having wide application. Moreover, high refractive index glasses where the TeO_2–B_2O_3 system is one part of them, were obtained. Simultaneously, the phenomenon of stable and metastable phase separation [4, 7], which is generally characteristic of glass-forming systems free of modifier oxides [8, 9], has also been observed. A number of properties, namely the glass-formation region [4, 10], density [5, 3], coefficient of thermal expansion [5], and optical constants [3–5], have been investigated successfully in the TeO_2–B_2O_3 system. No results on structural investigations of the tellurite borate glasses have been reported in the literature. It is in this context that the behaviour of the immiscibility and the composition of the separated phases in the TeO_2–B_2O_3 (K_2O) system [11, 12] have been studied.

The present study was undertaken in order to throw some light on the temperature dependence of the immiscibility; the coexisting phases and its compositions (phase diagram); the physical properties of the glasses obtained, as well as a structural interpretation of the glasses, on the basis of B^{11} nuclear magnetic resonance (NMR) spectra in the system [13].

2. Experimental details

2.1. Materials and glass preparation

The raw materials used (TeO_2 and H_3BO_3) were of Analar Grade. The batches were melted at a maximum temperature of 1123 K in a carborundum rod furnace, in a gold crucible, to determine the glass-forming ability and produce glasses suitable for determination of the physical properties, and glasses for differential thermal analysis (DTA) study. The melting time was about 2 h (in air at atmospheric pressure), where glasses were inten-

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sively homogenised. At about 973 K the glasses could be poured into a heated graphite mould and cooled down from 673 K at a rate of ~ 1 K min^{-1}.

2.2. Methods

The data for the equilibrium diagram were received from dynamic DTA measurements of samples, which were tempered in a different way. DTA was carried out up to 1273 K with a calibrated Pt/Pt–Rh thermocouple. Aluminium oxide heated above 1473 K was used as a standard. The heating rate was 4 K min^{-1}, suitable for a precise identification of the phase transitions. All DTA experiments were carried out on a 1500° C MOM-Budapest type derivatograph. X-ray powder diffraction patterns were obtained on a TUR-M62 X-ray diffractometer using Cu$K\alpha$ radiation.

To characterize the temperature dependence of the wide region of immiscibility in the system, three different techniques had to be used.

Method A: separation of the liquid phases in the melts with the help of a high temperature bottom centrifuge [11].

Method B: (i) cooling of the melts with a cooling rate of about 15 K sec^{-1}; (ii) cooling of the melts at a rate of about 150 K sec^{-1}.

Method C: cooling with rotating copper rollers at a cooling rate $\geq 10^3$ K sec^{-1}.

The glasses obtained (the homogeneous, as well as the separated vitreous phases) were analysed and studied using a scanning electron microscope (SEM), JSM-U3, using the standard technique.

The density was determined by weighing hydrostatically polished glass specimens in CCl_4 to within an accuracy of $\pm 5 \times 10^{-3}$ g cm^{-3}. The thermal expansion coefficient (α), the glass transition temperature (T_g), and the softening point (T_s) were dilatometrically determined, according to TGL 94-06009 [14]. The transmittances ($\lambda\tau_i$) in the ultraviolet (UV) and visible (VIS) regions were taken down with samples (of thickness 10 mm) exhibiting precisely flat parallel grains with the help of a SPECORD UV–VIS Carl–Zeiss Jena spectralphotometer.

Refractive indices were measured using the method of minimum angle of deviation by a Hilger and Watts goniometer at the following wavelengths: 404.66, 435.84, 479.99, 546.07, 587.56 and 643.85 nm.

The B^{11} NMR spectra were obtained in a KRB 35/62 (GDR) type spectrometer operating at 21 MHz in a wide-line regime. The modulation frequency was 70 Hz at an amplitude of 0.1 mT. For the B^{11} NMR measurements we chose three transparent, high optical quality glasses from the G region; subregion b in the GFR in Fig. 1.

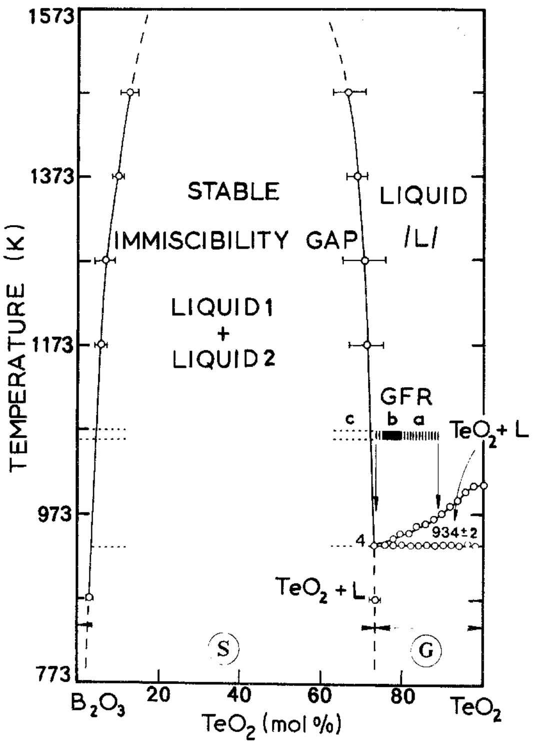

Figure 1 Phase equilibrium diagram of the TeO_2–B_2O_3 system. The GFR is composed of subregions: a – from 88.2 to 73.6% TeO_2, b – homogeneous liquid producing clear glass from 80 to 75% TeO_2, and c – glass and liquid with microheterogeneous structure; four – invariant point; G region without phase separation at normal conditions; and S region of compositions with high tendency of immiscibility.

3. Results

The system was investigated by 30 geometric points at intervals of 5, 3 and 2%* depending on the composition and its distribution in the G or S regions. The most probable disposition of the fields of the preliminary crystallization is presented in Fig. 1. The monotectic temperature was determined by DTA to be 934 K. An invariant point corresponding to a composition with 73.6 ± 0.5% TeO_2 was found; from its location the system could be treated as a composite of two quite different

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*All correlations between the components are given in mol %.

TABLE I Characteristics of the glass samples

Index	Composition (mol %)				Visual and REM characteristic
	TeO_2	B_2O_3	TeO_2	B_2O_3	
TB-1	80.0	20.0	80.3	19.7	transparent glass
TB-2	77.5	22.5	77.7	22.3	transparent glass
TB-3	75.0	25.0	75.1	24.9	transparent glass
	by synthesis		by chemical analysis		

regions, marked G and S in Fig. 1. In the TeO_2-rich part of the system an exact determination of the GFR was made, whereas in the a subregion, at a cooling rate of about $10\,K\,sec^{-1}$, we obtained glasses completely free of crystals (100 g batches), whereas they were yielded in the b subregion at a cooling rate of about $1\,K\,sec^{-1}$. Above 80% TeO_2 partial crystallization of the melts occurs, namely α-TeO_2.

In the B_2O_3-rich part of the system (region S) there is a stable miscibility gap (MG). The glass melts, which were prepared by different methods and frozen in by different temperatures, show a distinct separation into two vitreous phases; namely a transparent glass and an opaque glass phase with low density. With increase in temperature the dense phase will become more and more unstable. A selection of the replica electron microscope (REM) photographs are shown in Fig. 2, in which the degree of phase separation is clearly seen.

In addition there was a melt prepared of composition 60% TeO_2 and 40% B_2O_3 by method C. Fig. 3 shows a photograph of a light transmitted illumination of a glass type. It consists of clear glass in the middle part (arrow 1) and an opaque glass phase in the edge area (arrow 2) of the sample. The distribution of the elements in the sample, measured by X-ray microanalysis (Te $L\alpha$, β), shows an accumulation of about 80% tellurium in the middle part and a diminishing quantity in the edge area (about 4% tellurium).

Table I shows that the chemical composition of the glasses, prepared in the b subregion, is nearly the same as that of the batches. Results on some properties of selected glasses in the same region are presented in Tables II and III.

The B^{11} NMR studies indicate clearly the appearance of boron in both 3 and 4 coordination. No sign of formation of nonbridging oxygen in relation to the boron atoms is to be seen. More detailed information and discussion about B^{11} NMR measurements are given in [13]. Here we have used these results to make a structural interpretation of the binding and the random nature of the glass network.

4. Discussion

4.1. Phase diagram and immiscibility

It is known that in relation to the glass-former the monotectic temperature (temperature of the monotectic, i.e. isotemperature line where we have phase equilibrium between two liquids and a solid state phase in a binary system) is either above or below the melting point of the glass-former. When it is above, we have an idealized two-component glass-forming system in which a stable immiscibility gap occurs [15]. In this case, the monotectic temperature lies between the melting point of the glass-former and a second glass-former (i.e. B_2O_3 with a m.p. of 723 K [16]) beyond the immiscibility gap. It should be noted that many borate and silicate systems with an immiscibility gap behave in the same way. For example, for the binary B_2O_3–R_mO_n systems (where R_mO_n = MgO, CaO, BaO, ZnO, CdO, ThO_2, Sc_2O_3, La_2O_3, Bi_2O_3, Nb_2O_5) and SiO_2–R_mO_n (where R_mO_n = TiO_2, Cr_2O_3, Sc_2O_3, Dy_2O_3, Er_2O_3, Yb_2O_3 and Lu_2O_3) [17] beyond the immiscibility gap, the eutectic is on the glass-former side of the gap. From the above, binary system closer to the phase relations in the TeO_2–B_2O_3 system could be considered to be B_2O_3–Nb_2O_5 and SiO_2–Cr_2O_3 systems. Following the phase distributions, according to these systems, below the monotectic temperature we could construct the phase diagram shown in Fig. 4. The chemical incompatibility between the two mutual glass-formers in the system favours bonding at simultaneously structural preservation of their own networks, i.e. a space structural differentiation of the polyhedra takes place. This coeffect of the two glass-formers begins at a critical point, which for tellurite systems have been assigned to be at a concentration of 26 ± 5% second glass-former [9, 18, 19]. On the other hand, this space structural differentiation of the

TABLE II Properties of the glasses obtained

Index	Density, ρ (g cm^{-3})	Transformation temperature, T_g (K)	Softening point, T_s (K)	Coefficient of thermal expansion, $\alpha \times 10^7$ (K^{-1})	Transmittance in UV and VIS regions ($\lambda\tau_{i10}$, $\lambda\tau_{i50}$)nm (400, 500, 600 nm)%					Hardness values (kg mm^{-2})
TB-1	4.937	605	614	156	378	390	80	98	99	327
TB-2	4.810	614	625	147	375	387	82	98	99	345
TB-3	4.689	619	630	142	372	385	84	98	99	–

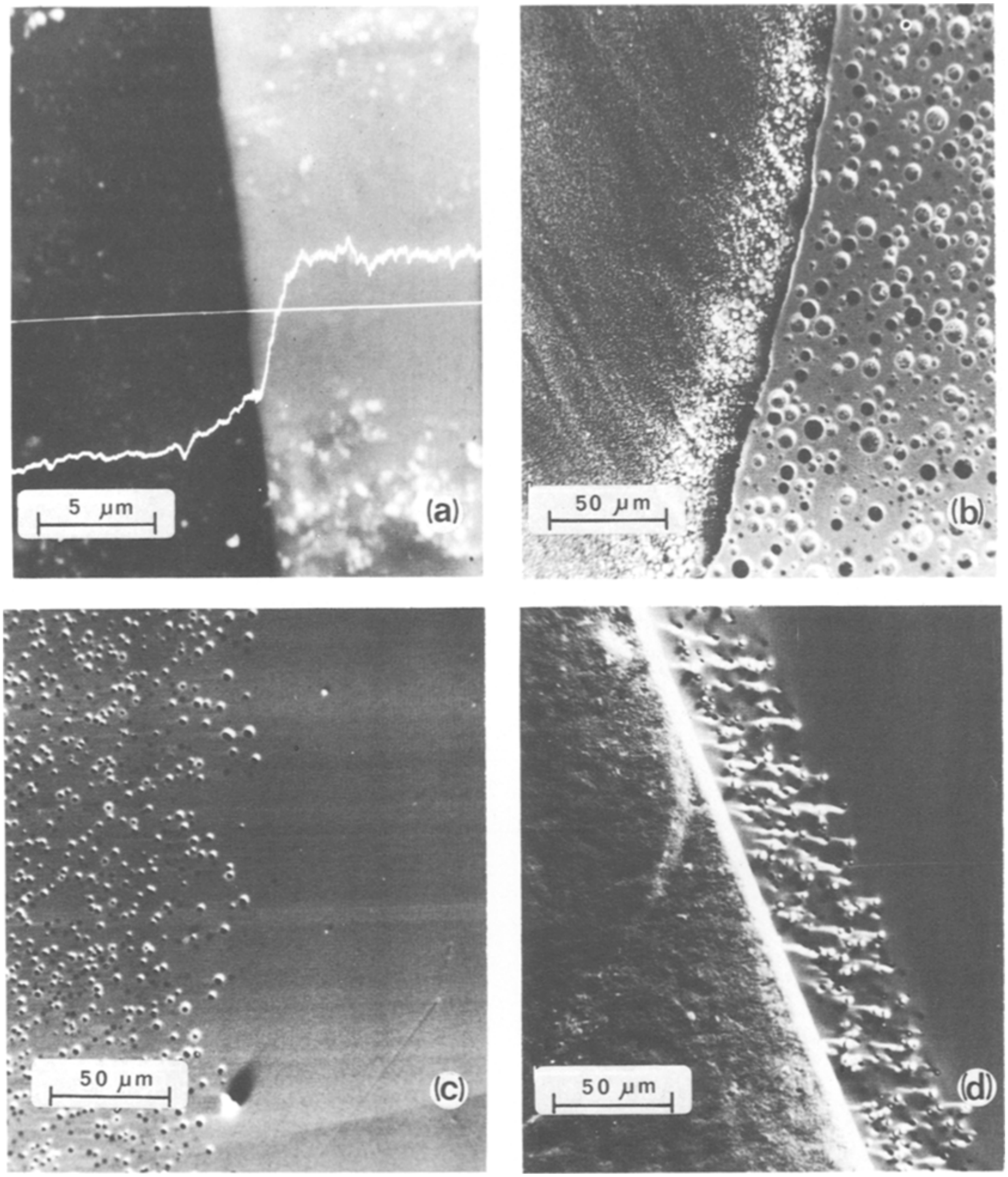

Figure 2 REM photographs: (a) phase boundary layer of a separated glass at 873 K of the composition with 20% TeO_2, 80% B_2O_3 obtained by method A; (b) phase boundary layer of a sample with 50% TeO_2 cooled at 1373 K after method B; (c) TeO_2-rich phase with nuclear phase separation of the glass with 60% TeO_2, 40% B_2O_3 obtained by method B; and (d) boundary diffuse layer of a sample with 35% TeO_2, 65% B_2O_3 produced by method B.

TABLE III Index of refraction and dispersion of the glasses

Index	Relative index value						Abbe number, ν_e	Main dispersion, $n_{F'} - n_{C'}$	Relative dispersion	
	n_h	n_g	$n_{F'}$	n_e	n_d	$n_{C'}$			$P_{g,F'}$	$\Delta P_{g,F'}$
TB-1	2.1191	2.0904	2.0621	2.0349	2.0233	2.0112	20.3	0.0509	0.557	0.016
TB-2	2.0934	2.0658	2.0386	2.0125	2.0013	1.9898	20.8	0.0487	0.558	0.019
TB-3	2.0676	2.0416	2.0157	1.9910	1.9803	1.9694	21.3	0.0465	0.553	0.015

basic building units leads to suppression of any binary compound formation*. In our case, the formation of any compound in the system has not been established. It should be emphasized that the stable liquid immiscibility in a wide region of the composition in the system is typical evidence for incompatibility between compound formation and liquid phase separation.

It was established that in region G the liquid curve shows a slight sigmoidal effect (see Fig. 1). This effect could be explained by the fact that metastable immiscibility gap (MIG) lies under the monotectic temperature in the TeO_2-rich region [23–25]. A great number of glass tempering tests below 936 K, produced in subregions a and b in a gold crucible, gave only crystal formation, as shown in Fig. 5. It is a logical consequence according to the phase diagram in Figs. 1 and 4. In the TeO_2-rich region we could not find subliquidus immiscibility under the monotectic line, described by Dimitriev and Kashchieva [7]†, extending widely into the region of glass-formation.

As is shown in Fig. 1, the TeO_2-rich branch of the binodal curve intersects the monotectic line in

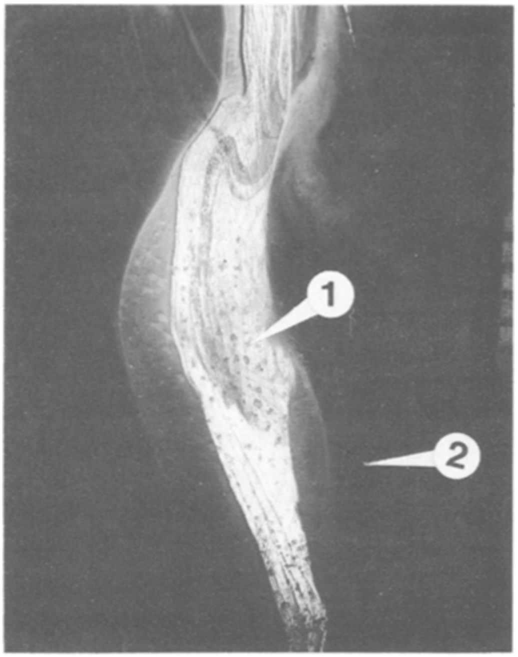

Figure 3 Photograph in transmitted illumination of a glass tape from region S, produced by method C, clear glass (arrow 1) and opaque glass phase (arrow 2).

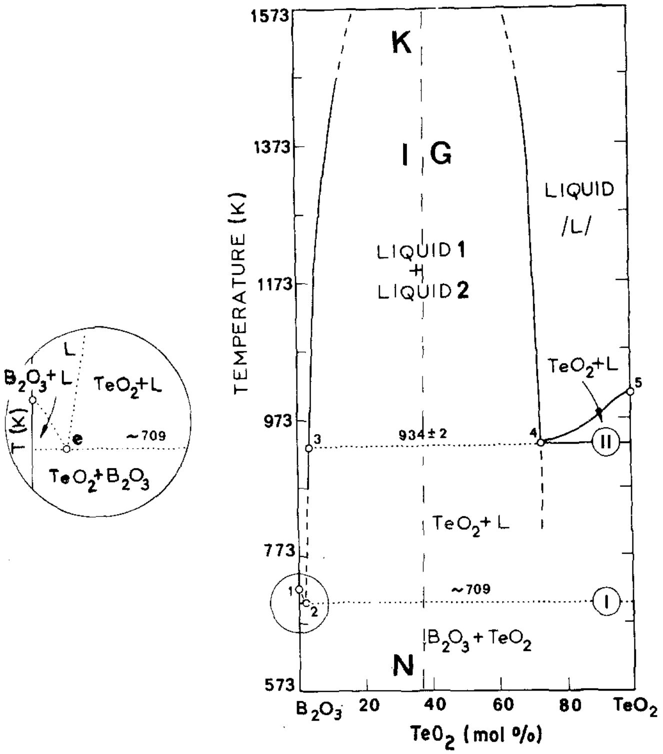

Figure 4 Phase distribution in the TeO_2–B_2O_3 system between 573 and 1573 K; point 1 – m.p. of B_2O_3; point two – eutecticum at ~ ⩽ 2% TeO_2, 98% B_2O_3; points three and four – nonvariant points, and point five – m.p. of TeO_2 (1006 K); line I is an isotherm at ~ 709 K, line II is the monotectic temperature, and K–N is an isopleth at 38% TeO_2, 62% B_2O_3.

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*Only a few cases of oxide compounds melting into two liquids have been reported in the literature [9, 20–22].

†The authors state that investigations are carried at nonequilibrium conditions, without cooling speed control, and that this is the cause of non-reproducibility of the results obtained in [7].

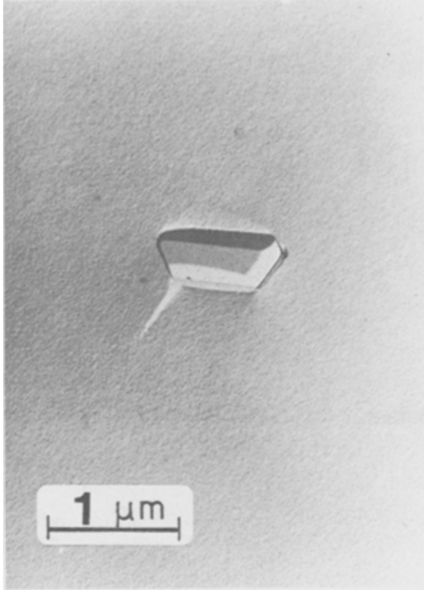


Figure 5 Crystals of α-TeO_2 in the glass composition 75% TeO_2, 25% B_2O_3 after thermal treatment at 773 K, 30 min.

an invariant point at 73.6% TeO_2, the lower limit of the GFR and the boundary between regions G and S, simultaneously. At higher temperatures the range of stable immiscibility decreases, but simultaneously the margin of error of the analysed compositions increases as shown in Table IV. The lines connecting the coexisting liquid phases L1 and L2, i.e. conodes, are isothermal lines which decrease in length quite slowly with increase in temperature. An upper critical point on the binodal curve could not be found up to 1573 K. The boundary of stable immiscibility of the TeO_2–rich side rises steeply with temperature and is nearly sharp. Because of this quite steep character of the two branches of the binodal curve (Fig. 1) there is reason to suppose that T_k lies at high temperature. Because of the low melting point and high rate of evaporation (high partial pressure) of the constituents, it is not possible to determine T_k at present. After an approximation of the branches of the binodal curve, it could be suggested that T_k corresponds approximately to 38% TeO_2 (see Fig. 4, K–N path at 38% TeO_2).

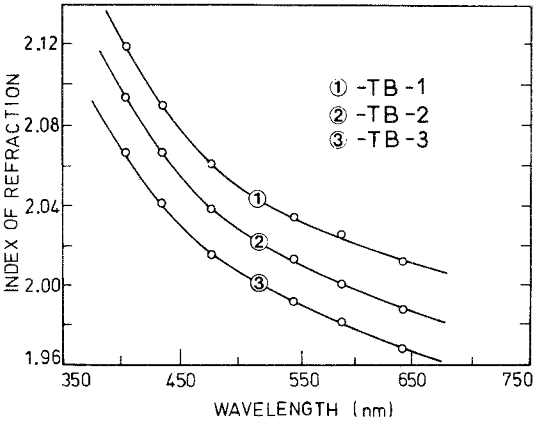


Figure 6 Optical dispersion curves for selected glasses.

4.2. Properties of the obtained glasses

The studies carried out up to now [4, 5] on the TeO_2–B_2O_3 system have only a tentative character. For this reason, it is of practical interest to carry out a detailed study of the glass properties of the system. Taking into account the above circumstances of the GFR and phase distributions (see Figs. 1 and 4), and as a second step, we investigated the properties of glasses in subregion b. The experimental results obtained are given in Tables II and III. It is seen that the density and linear expansion coefficient values increase smoothly with increase in the amount of TeO_2. The effect of change of index of refraction against wavelength is shown in Fig. 6. It has been established that the dependence of the index of refraction on the wavelength shows the effect of the B_2O_3 concentration; the refractive index, the coefficient of thermal expansion, the transmission and the density of the glasses increase with TeO_2 content. The values of transformation temperature and the softening point decrease, respectively.

As a result of the study of the GFR and the

TABLE IV Phase composition of liquids 1 and 2, obtained by chemical analysis in mol %

Temperature (K)	Liquid 1 (upper phase)		Liquid 2 (lower phase)	
	TeO_2	B_2O_3	TeO_2	B_2O_3
1473	12.1 ± 1.6	87.9 ± 1.6	66.2 ± 4.8	33.8 ± 4.8
1373	9.7 ± 1.1	90.3 ± 1.1	69.0 ± 1.0	31.0 ± 3.2
1273	6.7 ± 1.6	93.3 ± 1.6	70.6 ± 1.0	29.4 ± 4.8
1173	5.6 ± 0.7	94.4 ± 0.7	70.3 ± 1.0	29.7 ± 4.1
873	3.2 ± 0.3	96.8 ± 0.3	72.8 ± 1.0	27.2 ± 1.0

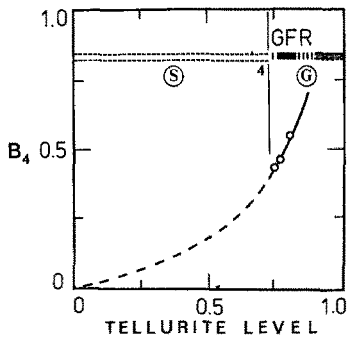


Figure 7 A room temperature correlation of tetrahedral boron against tellurite level and GFR (G and S regions).

optical constants of the glasses in this region, glasses with high optical quality have been developed, and optical constants are given in Table III. According to the nomenclature of the optical glasses these high-index binary optical glasses can be treated as super-heavy optical flint glasses.

4.3. Structure of the glasses

The nature and extent of boron coordination changes in alkali borate and alkali borosilicate glasses as a function of alkali oxide content has been the object of many (diffraction and spectroscopy) studies. The pioneer work of Bray and O'Keefe [26] who used NMR techniques, provided a quantitative estimate of the conversion of trigonal to tetragonal boron coordination as a function of the alkali level. On the other hand, Krogh-Moe and co-workers [27, 28] have shown that an alkali oxide addition to broron oxide initially forms pentaborate or tetraborate–boroxine units which are transformed, at higher alkali levels into diborate units.

Our preliminary structural investigation in the TeO_2–B_2O_3 system has been focused on the boron coordination state (natural abundance B^{11} = 81.17% and B^{10} = 18.83%) in the glasses. B^{11} NMR study shows that a significant fraction of the total boron concentration converts to tetrahedral coordination. The calculated fraction of boron in tetrahedral coordination (B_4) is shown in Fig. 7. The course of the curve, for example, is distinguished then from the curves of the calculated fraction of tetrahedral boron as a function of the per cent alkali in alkali borate and alkali borosilicates [29, 30]. It has been established that B^{11} in BO_4 building units in the TeO_2-rich glasses are uniform in comparison to B^{11} in the B_2O_3–GeO_2 [31] and B_2O_3–SiO_2 [32] systems.

There is a range of formation of simple structural units in the present system and it is shown in Fig. 8. In the TeO_2-rich part of the system we suppose building of $[-TeO_4-TeO_3-BO_4-]_\infty$ and structural interactions between BO_4 and BO_3 building units. We propose that the first mechanism of

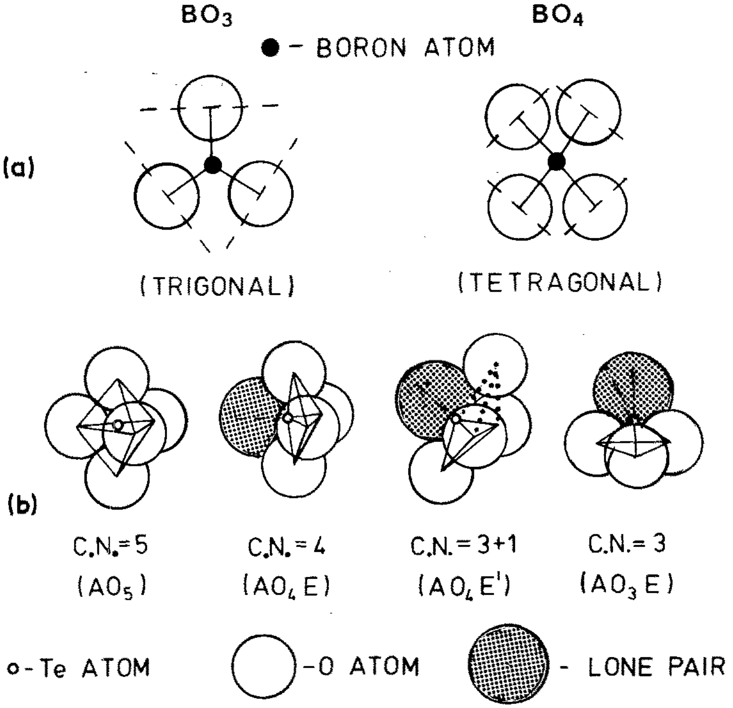
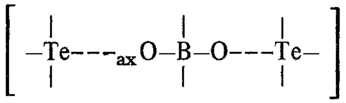


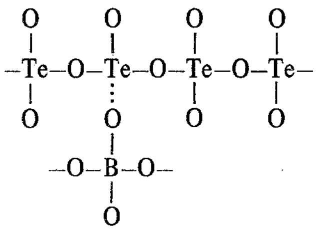
Figure 8 Boron (a) and tellurium (b) oxygen configuration of the building units in the glasses.

binding is based on the small line width of the central sharp B^{11} NMR peak of the glasses. Following the conclusions of [18, 19] it is assumed that the dynamic O_{ax} atoms (ax denotes axial bond) in the TeO_4 units play an important role in the realization of secondary bonding and building of BO_4 units. The number of tellurium atoms in the TeO_2-rich glasses which take part in the bonds of the type



$$\left[-\underset{|}{\overset{|}{\mathrm{Te}}}---{}_{\mathrm{ax}}\mathrm{O}-\underset{|}{\overset{|}{\mathrm{B}}}-\mathrm{O}---\underset{|}{\overset{|}{\mathrm{Te}}}-\right]$$

is relatively small. For example, at a composition of 80% TeO_2 and 20% B_2O_3, our calculations show that approximately 9% of the TeO_2 building units (after an elongation of part of the axial bonds) satisfy the coordination ability of B^{3+} in BO_3 to a conversion into BO_4 polyhedra. By this way of binding we suppose that a "compromiser oxygen bridge" satisfies the coordination states of both tellurium (3 or 3 + 1) and boron (4) atoms as is shown in Fig. 9. It is a logical consequence of this way of binding, where the field strength ($F_P = 2.0$, $F_{B_3} = 1.62$, $F_{B_4} = 1.42$, $F_{Te} = 1.0$) of the tellurium atoms is lower than that of the B_3 or B_4 state. Because of small ionic radius of boron, the boron ions have strong electrostatic fields and both the BO_3 and BO_4 groups are characterized by a considerably more compact and stable structure than the tellurium–oxygen building units in the vitreous network. In that way at equal conditions a small amount (approximately a fourth degree smaller) of TeO_4 units is incorporated into the B_2O_3–rich upper phase (see data from the Table IV). On the basis of our experiments and the chemical nature of the constituents (anhydrides of acids, character and differences in ionic field strengths, electrostatic bond strength, etc.) we suggest building of triborate and diborate structural fragments, surrounded by parts of



chains. The character of the bonding between two mutual glass-formers is significantly affected by the acidity. It seems that the acidic character of the second glass-former is of great importance in the formation of a two-liquid phase structure of the tellurite glasses [9, 18, 19].

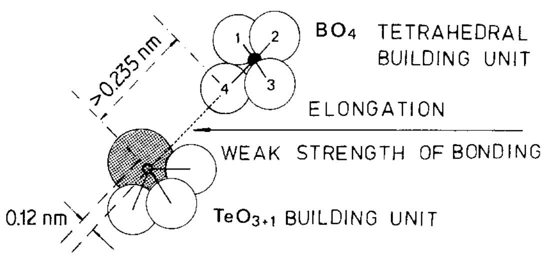


Figure 9 Model illustrating the method of secondary bonding of TeO_3 (TeO_{3+1}) and BO_4 structural units, as well as the conversion of BO_3 to BO_4 atomic arrangement through the oxygen atom (4).

5. Conclusions

The results obtained may be summarized as follows.

1. The phase equilibrium in the TeO_2–B_2O_3 system has been investigated. The phase determinations showed that the binary system is a simple eutectic, without formation of any compounds. A wide region of the stable miscibility gap (from 3.9 to 73.6% TeO_2 at isothermal cut at 873 K) has been determined. A metastable immiscibility gap below the monothetic temperature could not be found in the TeO_2-rich part, irrespective of the fact that the liquidus shows a slight sigmoidal shaped effect.

2. The temperature dependence of the stable phase separation in the system has been studied. An upper critical point of the immiscibility dome could not be found up to 1573 K. The chemical analysis of L1 and L2 liquids shows that they are microheterogeneous irrespective of the quite high cooling rate of the melts. A complete separation of the phases is not possible, even by use of high-temperature centrifuge.

3. The TeO_2-rich glasses are microhomogeneous and a weak crystallization ability of the glasses was found in subregion b of the glass-forming region. A monotectic temperature at 934 ± 2 K and a nonvariant point at 73.6% TeO_2 has been established, above which an immiscibility gap is observed. Our assumption [9, 19] that in the tellurite systems with a second glass-former there should be stable immiscibility starting with a critical composition within the limits 26 ± 5% second glass-former, was validated in this system.

4. A number of physical and chemical properties of the TeO_2-rich glasses have been investigated.

The refractive index, the linear expansion coefficient and the density increase with the amount of TeO_2, but the values of transformation temperature and softening point decrease.

5. B^{11} NMR spectroscopy investigation indicated that boron atom in the glasses exists in two coordination states. The amount of the BO_4 tetrahedra is approximately 50% of the boron fraction of a glass composition, and sharply increases with increase of the TeO_2 contents. At coordination BO_3 to BO_4 transition we supposed that only a little fraction of the tellurium atoms take part in the coordination boron conversion. In the TeO_2-rich region we assumed building fragments like triborate or diborate groups surrounded by TeO_3 and TeO_4 units of tellurium–oxygen chains, whereas in the B_2O_3-rich region building groups of boroxine units are indicated.

References

1. M. IMAOKA, in "Proceedings of the 6th International Congress on Glass" (Washington DC, 1962) p. 150.
2. M. IMAOKA and T. YAMAZAKY, *J. Ceram. Assoc. Jpn.* 76 (1968) 160.
3. A. YAKHKIND, *J. Amer. Ceram. Soc.* 49 (1966) 670.
4. W. VOGEL, H. BÜRGER, G. WINTERSTEIN, CH. LUDWIG and W. JACKEL, *Silikattechnik* 25 (1974) 209.
5. J. STANWORTH, *J. Soc. Glass Technol.* 38 (1954) 183, 425.
6. *Idem, ibid.* 36 (1952) 217.
7. Y. DIMITRIEV and E. KASHCHIEVA, *J. Mater. Sci.* 10 (1975) 1419.
8. R. CHARLES and F. WAGSTAFF, *J. Amer. Ceram. Soc.* 51 (1968) 16.
9. V. KOZHUKHAROV, M. MARINOV and J. PAVLOV, *J. Mater. Sci.* 13 (1978) 997.
10. O. MAZURIN, M. STRELTSINA and I. SHVAIKO-SHVAIKOVSKAYA, "Svoistva Stekol i Stekloobrazuyushchikh Rasplavov" Vol. 2 (Nauka, Moscow, 1975) p. 320.
11. H. BÜRGER, L. HORN, W. JAEKEL and W. VOGEL, *Silikattechnik* 32 (1981) 177.
12. H. BÜRGER, J. HOFFMANN and W. VOGEL, *ibid.* 34 (1983) in press.
13. R. GÖRING, H. BÜRGER, H. NASS and B. SCHNABEL, *Phys. Status Solidi (a)* 68 (1981) K29.
14. TGL-94-06009, in "Taschenbuch Glas", edited by H. Marusch (VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1978) p. 155.
15. E. LEVIN, *J. Amer. Ceram. Soc.* 50 (1967) 29.
16. G. SAMSONOV *et al.* "Physicochemical Properties of Oxides" (Metalurgia, Moscow, 1978) p. 68.
17. N. TOROPOV, V. BARZAKOVSKII, V. LAPIN and N. KURTSEVA, "Diagramii sostoyania Silikatnih Sistem" Vol. 1 (Nauka, Leningrad, 1969) pp. 91–196.
18. S. NEOV, I. GERASIMOVA, V. KOZHUKHAROV and M. MARINOV, *J. Mater. Sci.* 15 (1980) 1153.
19. V. KOZHUKHAROV, H. OEL and B. CAMARA, *Glastechnische Berichte* 54 (1981) 292.
20. D. RASE and G. LANE, *J. Amer. Ceram. Soc.* 47 (1964) 48.
21. I. BELYAEV, *Zhurn. Fiz. Khim.* 30 (1956) 1419.
22. K. KIM and F. HUMMEL, *J. Amer. Ceram. Soc.* 42 (1952) 286.
23. R. ROY, in "Advanced Nucleation of Crystalline Glass" (Glass Division of the American Ceramic Society, Columbus, Ohio, 1971) p. 51.
24. W. VOGEL, "Glas-chemie" (VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1979) p. 118.
25. I. GUTZOW, *Comtemp. Phys.* 21 (1980) 253.
26. P. BRAY and J. O'KEEFE, *Phys. Chem. Glasses* 4 (1963) 37.
27. S. SVANSON, E. FORSLIND and J. KROGH-MOE, *J. Phys. Chem.* 66 (1962) 174.
28. J. KROGH-MOE, *Phys. Chem. Glasses* 6 (1965) 46.
29. R. ARAUJO, *ibid.* 20 (1979) 115.
30. R. ARAUJO, private communication (1980).
31. J. BAUGHER and P. BRAY, *Phys. Chem. Glasses* 13 (1972) 63.
32. R. GÖRING and H. NASS, *Phys. Status Solidi (a)* to be published.

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