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Phase equilibria and immiscibility in the TeO_2-P_2O_5 system

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The phase equilibria and immiscibility of mutual glass formers up to 50 mol % P_2O_5 have been studied. Phase analysis indicates the formation of three new phases – incongruent melting $Te_4P_2O_{13}$, $Te_2P_2O_9$, and a supposed metacompound. Electron microscope investigations established stable and metastable phase separation. The immiscibility confines the tendency to glass formation up to 25.8 mol % P_2O_5. A reliable interpretation in relation to the morphology of liquid–liquid immiscibility and crystallization is considered.

1. Introduction

According to Stanworth [1, 2] tellurium dioxide was predicted to be a glass former on the basis of the electronegativity of its cation. This was confirmed experimentally by a significant number of binary and ternary TeO_2 systems [3–6]. So far a phase separation has not been established in TeO_2–M_nO_m systems, where M_nO_m is an alkaline or alkali earth oxide, typical of vitreous silicates and borous systems [7–9]. The problem is of further significance in relation to the immiscibility characteristics of tellurium dioxide in a system of other glass formers [6, 10]. If immiscibility can be experimentally observed in these systems, then each ternary system TeO_2–G_nO_m–M_nO_m, where G_nO_m is a glass former, would exhibit an immiscible dome.

This study was undertaken to explore the existence of immiscibility and binary compounds in the TeO_2–P_2O_5 system (in air at atmospheric pressure) in connection with further research on the interpretation of the structure and physicochemical properties of tellurium dioxide glasses. With a view to the above problems, our knowledge of phase equilibrium could be of significant importance.

2. Experimental procedure

The raw materials (TeO_2 and P_2O_5) were of AnalaR grade. In almost all cases the accurately weighed mixtures were slowly heated to about 450° C in air in porcelain crucibles to produce 10 g glass. These calcined batches were then melted in an electric furnace with dry air as the furnace atmosphere for 15 to 20 min at 800 to 950° C depending on the composition. The homogeneous meltings produced are easily cooled as transparent glasses. Because of the danger of TeO_2 and P_2O_5 loss due to vaporization, all glasses with a content above 30%* P_2O_5, as well as all stoichiometric compositions, were melted in non-air-tight quartz glass ampoules. The latter were cooled to room temperature by immersion in water. This avoided losses due to volatility at the melting temperature. A liquid–liquid phase separation was observed visually with increase in the P_2O_5 concentration.

Differential thermal analysis (DTA), X-ray diffraction, and optical and electron microscopy were used to identify phases and immiscibility. DTA was carried out up to 900° C with a calibrated Cr–Al thermocouple. Aluminium oxide heated up to 1200° C was used as a standard. The heating rate was $10°\,C\,min^{-1}$ on 150 mg glass or polycrystalline samples placed in a special profiled crucible (Au + 15% Pd alloy). Control samples and all stoichiometric compositions have also been tested on ORION GYEM type derivatograph.

X-ray powder diffraction patterns were obtained on a TUR-60M X-ray diffractometer using CuKα

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

TABLE I Morphology and optical properties of the phases in the system

Morphology and optical properties	Phases $Te_4P_2O_{13}$	$Te_2P_2O_9$	TeP_2O_7
Habit	Long prismatic sub-parallel crystals and irregular grains	Long prismatic and xenomorphic cuts	Scaly crystals
Symmetry	Monoclinic	Rhombic	Monoclinic (?)
Cleavage	One direction	Absent	Basal (0 0 1) (?)
Colour and Pleochroism	Ng-dark yellow Nm-yellow Np-light yellow	Yellow	Light yellow or uncoloured
Refractive index	> 1.78	> 1.78	Np = 1.774 Ng > 1.780
Extinction	Parallel and inclined (c:Ng = 8°)	Parallel	Parallel and inclined
Optical character	Positive	Positive	
2V	40 to 50° (?)	70 to 75° (?)	

radiation. Optical examination of the samples was performed in plane polarized light. The freshly fractured surfaces of part of the samples were etched by 2%HF for 10 sec and carbon–platinum replicas were precipitated. The observations were carried out with a ZEISS ELMI-D2 electron microscope and JEOL JEM IOOB in scanning condition using the standard screen technique by means of thin gold sputtered film.

3. Experimental data

Hardened vitreous samples were used in order to obtain primary DTA information. It was established that all glass samples up to 30%P_2O_5 possess a marked exothermic crystallization effect and a strongly dynamic endothermic effect with raising of P_2O_5 concentration. A dynamical change of exothermic effects is also present from 400° C. The critical temperature of the metastable immiscibility gap (MIG) corresponding to 495° C is established at a composition with 22%P_2O_5*.

3.1. Crystalline phases

The study of the phase relations in the system revealed the existence of three intermediate crystalline phases: $Te_4P_2O_{13}$, $Te_2P_2O_9$ and TeP_2O_7. Compositions up to 10%P_2O_5 possess only one crystalline phase – paratellurite. By increasing the P_2O_5 content a new compound ($Te_4P_2O_{13}$) forming long prismatic crystals with one cutting direction appears (Fig. 1). TeO_2 and P_2O_5 taken in molar ratio 2:1 formed $Te_2P_2O_9$, also with a prismatic habit. With the P_2O_5-rich

Figure 1 Prismatic $Te_4P_2O_{13}$ crystals.

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*The interpretation of phase separation established by DTA will be published separately.

TABLE II Lattice spacings, d, and relative intensities of the compounds

$Te_4P_2O_{13}$		$Te_2P_2O_9$		TeP_2O_7	
d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
6.11	25	6.51	5	5.98	5
4.69	5	6.24	5	4.75	50
4.42	20	5.40	20	4.05	100
4.29	15	4.98	5	3.71	5
3.97	10	4.60	25	2.66	15
3.66	90	3.92	30	2.62	15
3.57	100	3.80	100	2.44	15
3.31	25	3.40	60	1.961	10
3.11	10	3.17	20	1.945	5
3.07	100	3.02	100	1.926	5
2.91	15	2.97	30	1.903	10
2.54	50	2.78	20	1.817	20
2.31	80	2.57	25	1.804	10
2.20	10	2.48	40	1.759	10
2.15	10	2.39	25	1.704	10
2.08	5	2.36	30	1.681	10
1.985	20	2.28	15	1.669	5
1.970	50	2.03	60	1.615	5
1.848	10	1.998	10	1.505	20
1.814	10	1.918	15	1.427	25
1.781	20	1.888	15	1.372	10
1.722	35	1.862	15	1.328	5
1.695	5	1.794	10	1.299	10
1.621	10	1.752	15	1.241	10
1.580	10	1.716	5	1.141	10
1.532	15	1.661	30	1.132	10
1.519	20	1.639	5		
1.475	5	1.610	15		
1.441	10	1.593	15		
1.397	10	1.575	15		
1.371	10	1.565	5		
1.287	5	1.499	5		
1.272	5	1.484	30		
		1.427	10		
		1.361	5		
		1.354	15		
		1.331	10		
		1.301	20		
		1.203	15		
		1.199	15		
		1.161	5		

compositions optical microscopy identified a new anisotropic scaly phase. Simultaneously, X-ray patterns were found showing lines different from those attributable to the above established phases. The formation of a metacompound may be assumed in the system. The presence of TeP_2O_7 is still not proven because of the high degree of hydration of its crystals and will be subject to further research. The optical properties of the phases are represented in Table I and diffraction patterns are given in Table II.

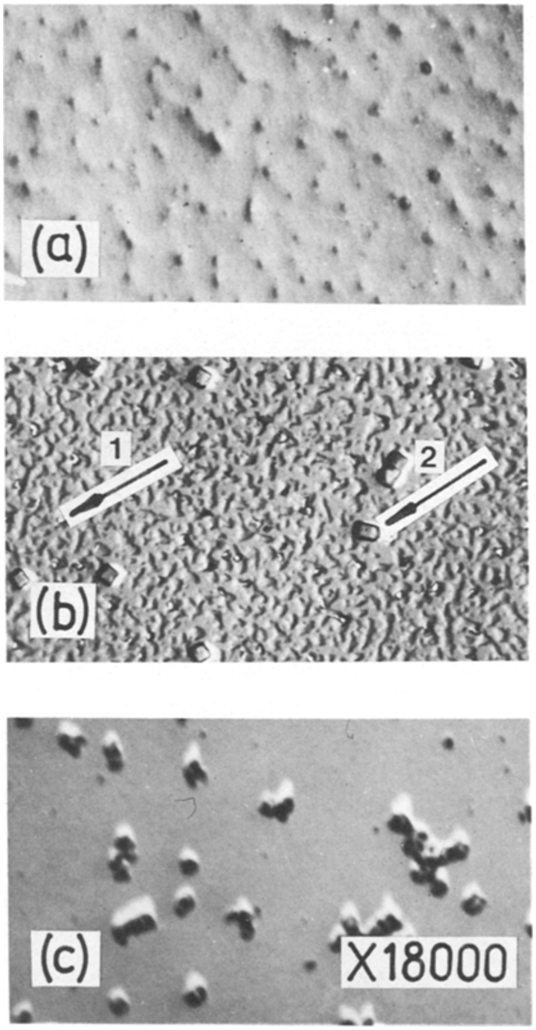


Figure 2 Replica electron micrograph (REM) of 90% TeO_2–10% P_2O_5. Samples exposed at (a) 375° C, 70 h; (b) 450° C, 19 h 20 min (arrow 1, crystal nucleus; arrow 2, TeO_2 crystals) and (c) 510° C, 12 h

3.2. Liquid–liquid immiscibility

The "anomalous" behaviour of glasses, possessing dynamic exothermic effects in fairly narrow limits of concentration, could be explained by the presence of MIG. Initial colourless glass, after additional thermal treatment in the subsolidus immiscibility gap, exhibits the Tyndall effect and is characterized by a micro-heterogeneous structure as shown in Fig. 2a. At higher temperatures (Fig. 2b) the phase separation is more clearly visible; crystal nuclei appear (Fig. 2b, arrow 1) and crystals of tellurium dioxide (Fig. 2b, arrow 2) can be seen. From the phase equilibria of other binary telluride systems described previously

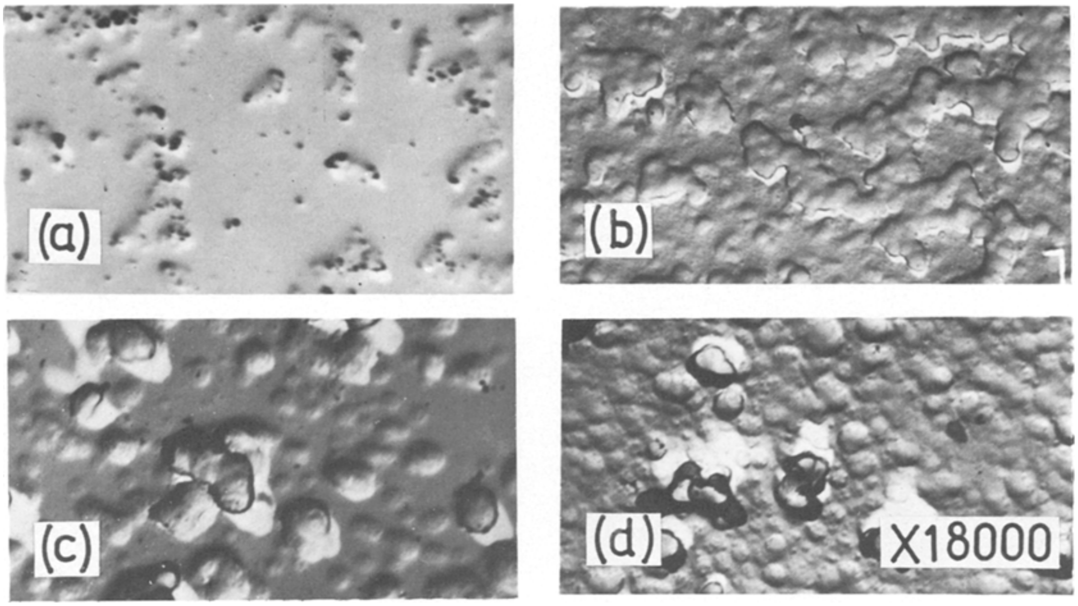


Figure 3 REM of 74% TeO_2–26% P_2O_5 glass composition. (a) No thermal treatment. The same sample exposed at (b) 400° C, 3 h (c) 510° C, 5 h and (d) 510° C, 12 h.

[11–13], it was established that tellurium dioxide crystallizes at about 400° C in the TeO_2-rich subsolidus region. In this system the exothermic effect of crystallization of TeO_2 falls in the MIG, being quite close to the phase boundary, but above it. Electron microscopy showed that the sample heated up to temperatures above the MIG phase boundary had a clear matrix, but developed a scale of structure illustrated in Fig. 2c.

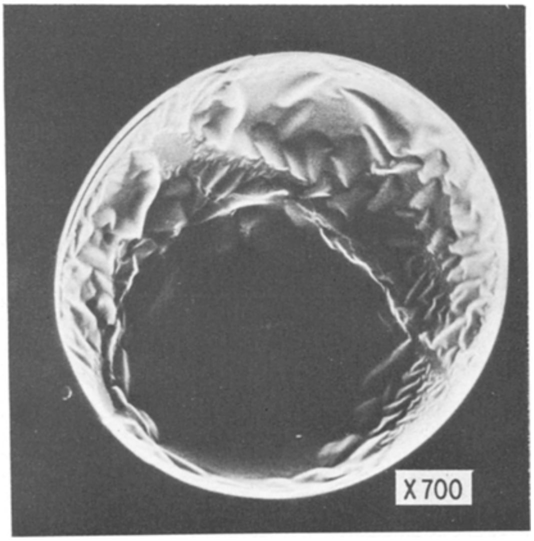


Figure 4 Scanning electron micrograph (SEM) of a drop (glass sample 66.6% TeO_2 – 33.4% P_2O_5) with a flown process of metastable sub-microcrystallization during cooling time. The small crystals in the habit are similar to the compound $Te_2P_2O_9$.

Hardened glass (Fig. 3a) has a slight orange colour and micro-heterogeneous structure. After thermal treatment the orange colouring is lost. For a given temperature within the MIG the scale of microstructure decreased with time along with the appearance of a greater number of smaller drops (Figs. 3c and d).

Initial glass with a composition corresponding to $Te_2P_2O_9$ has a micro-heterogeneous structure.

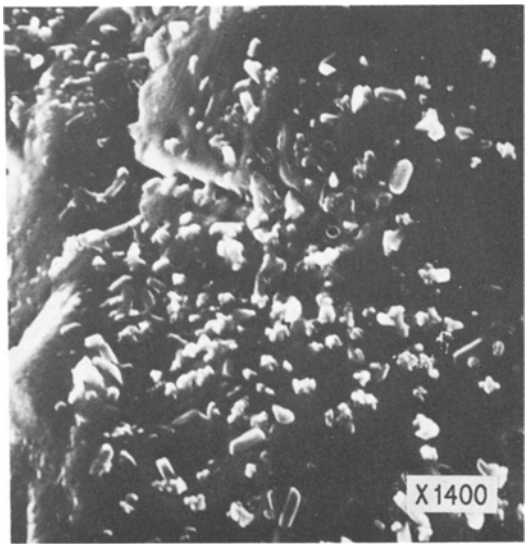


Figure 5 SEM of small crystals of the compound $Te_2P_2O_9$ on its mineral ground.

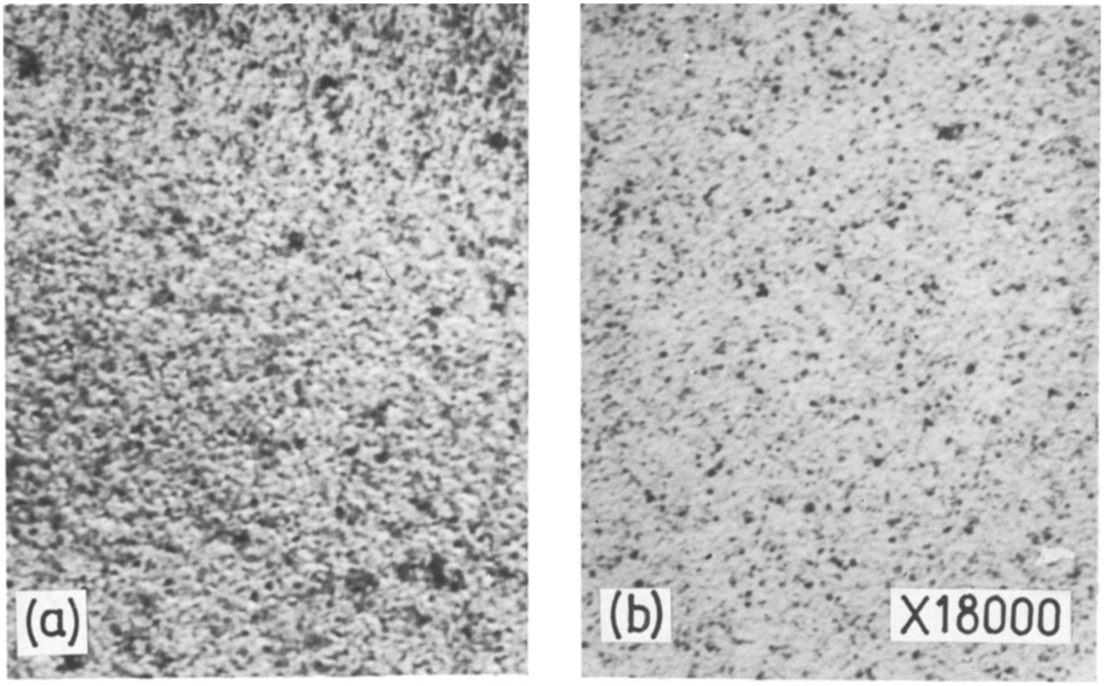


Figure 6 REM of (a) layer L1 and (b) Layer L2 of freshly broken surface without chemical treatment. The fine dispersion of the two phases can be seen. Layer L1 shows a Tyndall effect.

As shown in Fig. 7, a solid region of immiscibility (IG) is placed above its geometrical point. Accumulation of substance on the phase boundary of a drop as well as a process of sub-microcrystallization is well illustrated in Fig. 4. Here, the distribution of the phase is distinct, and similar to the $Te_2P_2O_9$-crystal habit (Fig. 5).

The glasses containing above 25%P_2O_5 are clearly micro-unhomogeneous. In these cases, we shall provisionally refer to liquid-layers L1 and L2, as they themselves are significantly micro-heterogeneous (Fig. 6). A two-phase structure in the IG develops very quickly, but there is a small difference between the two layers, the upper one being richer in P_2O_5, as found by chemical analysis, and showing a more marked Tyndall effect.

3.3. Phase equilibria

The most probable disposition of the fields of the primary crystallization, the presence of three incongruent compounds, regions of metastable and stable liquid–liquid immiscibility have been defined on the basis of experimental data (Fig. 7). The characteristics of the non-variant points are given in Table III. A subsolidus immiscibility gap has been found in the system (3 to 31%P_2O_5) intersecting the isopleth of $Te_4P_2O_{13}$. This phenomenon is almost unique as a simultaneous existence of metastable liquid phases and a compound. In the literature there is very little data for the intersection of MIG by isopleths of certain compounds [14–17].

A glass transition temperature of about 300° C was established. As is already known, the nature of

TABLE III Characteristic of the invariant points*

Point	Composition (mol %)		Phases in equilibrium	Characteristic	T (° C)
	TeO_2	P_2O_5			
e	90.8	9.2	$T + T_4P + L$	eutectic	520
n_1	85.0	15.0	$T_4P + T_2P + L$	peritectic	600
n_2	76.0	24.0	$T_2P + TP + L$	peritectic	670
n_3	74.2	25.8	$TP + L + L1 + L2$	peritectic	713

*$T = TeO_2$, $P = P_2O_5$ and L = liquid

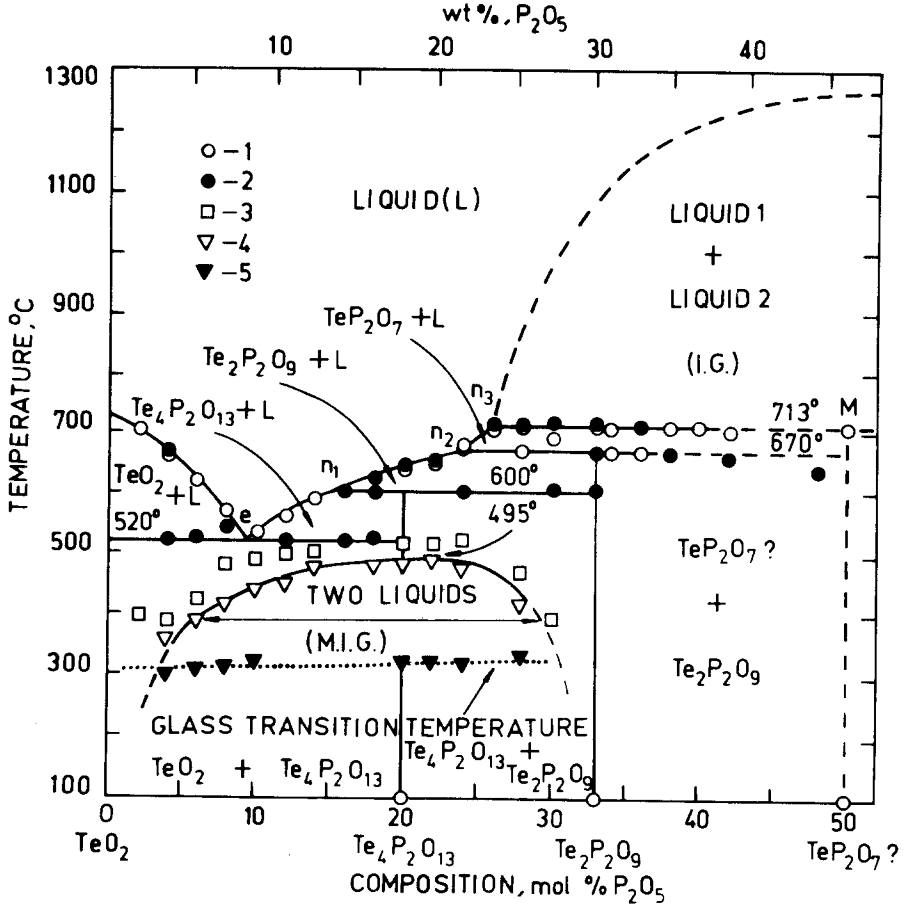


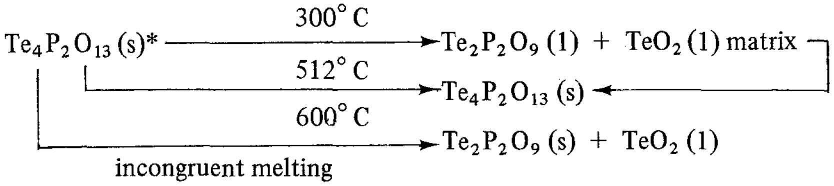
Figure 7 Phase diagram of the $TeO_2-P_2O_5$ system. 1, DTA data of glass for T_1; 2 DTA data of polycrystalline samples of T_1 and T_S; 3, exothermal effect of crystallization of the glasses; 4, initial stage of crystallization; 5, glass transition temperature.

the dispersed phases below this temperature cannot be identified as metastable immiscibility. Therefore, an approximate iso-viscosity curve was drawn; in the temperature region below it the development of a two-phase structure is thermodynamically inadmissible because of slowed down relaxation and kinetic interactions. The curve of the metastable boundary (Fig. 7) is slightly asymmetric and resembles that in the $B_2O_3-SiO_2$ system [18]. The critical temperature (495° C) corresponds to the composition 88%TeO_2–22%P_2O_5 and approximately coincides with prolongation of the IG boundary in the subsolidus region.

4. Discussion

According to the phase diagram in Fig. 7 the upper limit of homogeneous glass forming should be corrected only to 15%P_2O_5. Compositions outside but near the IG tend to separate metastably into two noncrystalline phases when heated at subsolidus temperature. Above point n_3 the liquid always separates itself into two layers proven as vitreous according to X-ray and electron microscopy studies. It can be concluded, therefore, that a stable IG limits the useful part of glass forming essentially within the range from 2 to 25.8% P_2O_5. The lack of a sigmoidal shaped effect in the liquidus curve could be explained by the fact that the MIG lies completely under a solidus isotherm.

Two incongruent melting compounds $Te_4P_2O_{13}$ and $Te_2P_2O_9$, as well as one supposed TeP_2O_7 have been proven. They melt at 600, 670 and 713° C respectively, as the latter decomposes itself into two liquids. The compound $Te_4P_2O_{13}$ metastable phase is separated between 300 and 490° C and possesses an exothermic effect of crystallization at 512° C. At the decomposition of $Te_4P_2O_{13}$ drops enriched with $Te_2P_2O_9$ are formed and distributed in a TeO_2-rich matrix. This interesting phenomenon could be expressed schematically as:



The incompatibility between formation of the compounds and liquid–liquid immiscibility is known. A typical example is the exeptionally high IG situated between the $B_2Tl_2O_4$ and $B_4Tl_2O_7$ compounds in the $Tl_2O-B_2O_3$ system [19]. Only a few cases of oxide compounds stratifying into two liquids have been reported in the literature [8, 20–22].

Further research on the mechanism and kinetics of the rearrangement process in the system are envisaged. Here, we shall only note that the process of liquid–liquid immiscibility is easily and quickly realized with no special thermal treatment. A larger phase separation was observed on the P_2O_5-rich side of the system. Over a wide temperature range a minimum in viscosity (increased mobility) may be assumed at low TeO_2 concentration. Mobility increases significantly, as a result of the character of the immiscibility shown in Fig. 8, point 10 (see also Fig. 6). Both liquid phases L1 and L2 are collinear for temperatures between T_c of the IG and 713° C. On the other hand at point M we have the equilibrium of two liquid phases combined with TeP_2O_7, i.e. incongruent melting of a compound with separation. Taking into account the free energy curve, the presence of three-phase equilibrium at point M allows us to conclude that the minimum of the free energy curve of the compound TeP_2O_7 probably will lie between the double minima of the liquid curve.

The phase separation and the crystallization in the system could be showed schematically as in Fig. 8. Using and enlarging the pattern of the stages of crystallization of non-homogeneous glass given by Roy [23], we can accept that it realizes itself in the following manner:

(1) High above the liquidus in I and II isostructure regions a stable homogeneous liquid easily fixed in vitreous state could be expected.

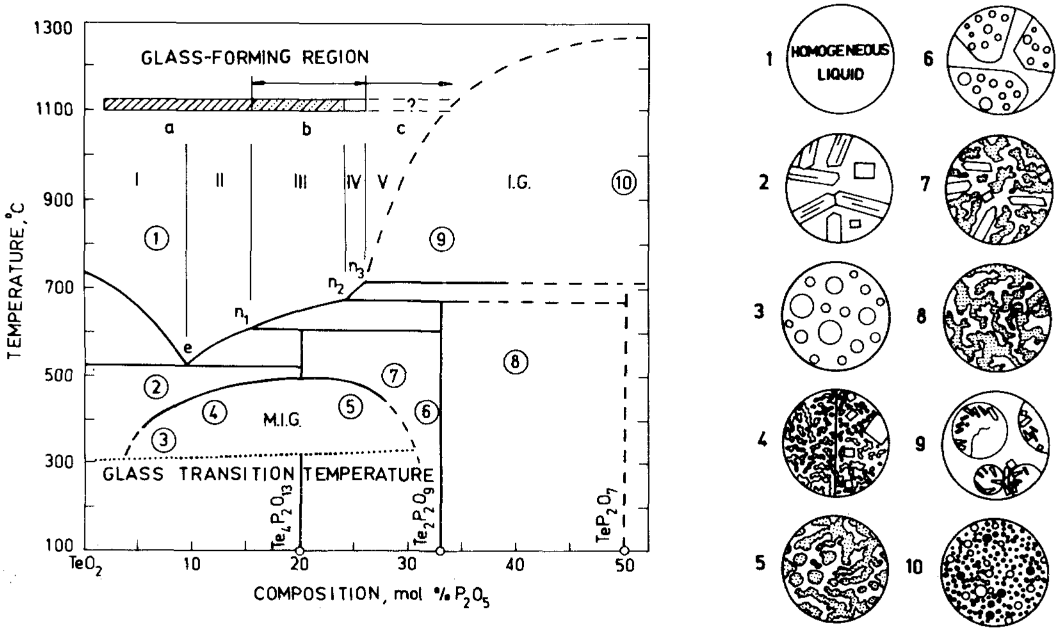


Figure 8 Schematic illustration of the morphology of phase separation and crystallization at ten most characteristic points, isostructure regions (I–V) and the correction of the glass forming region. Regions: a, homogeneous liquid producing clear glass; b, liquid with "special" structure and c, liquid with micro-heterogeneous structure.

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*(1) = liquid and (s) = solid state.

For liquids of regions II and III near to the liquidus, aggregates with size 50 to 100 Å could be expected, but they are of such an order that it could not be considered as a second phase. The glasses of regions III and IV will be characterized by a "special" structure i.e. with an extremely high dispersion of the existing liquid phases (Fig. 8, glass forming region "b"). The region V meltings cannot be fixed in a homogeneous state. The glasses of this region will always tend to a higher degree of micro-heterogeneity.

(2) With the decrease of temperature for numerous compositions of regions I, II, III, and IV we may have a development of the microheterogeneous structure with the size of the phases about 900 Å. Their development will occur after generation and running of disorderly nucleation. A sphere of diffused substance will be formed around the created nucleus, preceding the new phase. It is necessary for the development of the nucleus, as the next stage is the growth of the nucleus phase in a spherulitic manner in the matrix (Fig. 8, point 3). On the other hand, the metastable sub-microcrystallization in the specific region of composition into IG. can also be realized (Fig. 8, point 9). This observed phenomenon is of great significance and shall be the subject of detailed interpretation.

The liquid immiscibility is known always to precede the crystallization process in the subsolidus region. This, a metastable drop-like liquid phase, is still remaining alongside with the development of stable crystals. Under other conditions, a sub-metastable drop-like liquid phase was observed on the crystal surface, as seen in Fig. 9. Consequently the liquid immiscibility seems, in this case, to follow the crystallization process. Two possible explanations could be given for this quite surprising fact. On one hand, some above-stoichiometric quantities of the substance can probably not be included into the crystal lattice during the crystallization process; on the other, the liquid phase might be due to the two tendencies to crystallization and phase separation, which are strongly evident in the examined region (Fig. 8).

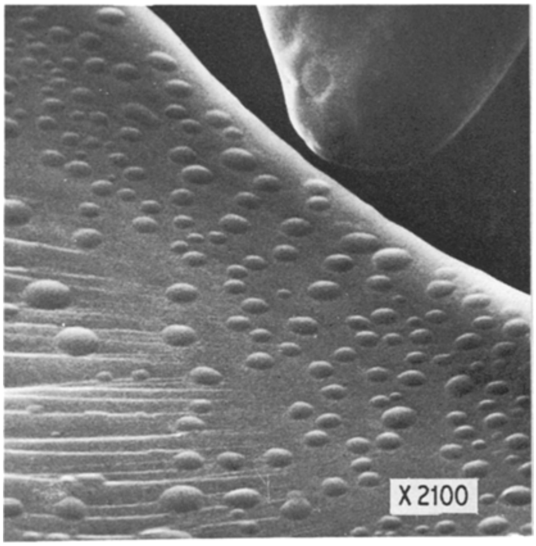

Figure 9 SEM of nonchemical treatment surface of $Te_2P_2O_9$ crystals illustrating surface subsolidus metastable liquid phase.

It is obvious that phase separation in the system is very complex. The exact nature of this phenomena needs detailed investigation and explanation.

5. Conclusion

The phase equilibrium in the system up to 50% P_2O_5 has been studied. The wide IG and MIG proved to limit glass forming up to 25.8% P_2O_5. Two new incongruent melting compounds, $Te_4P_2O_{13}$ and $Te_2P_2O_9$, as well as one compound for which the composition TeP_2O_7 is assumed, have been proven. It was shown that both the immiscibility gap and the metastable immiscibility gap cover wide regions in the phase diagram. Thus, the system can successfully be used in clearing up the process of phase separation of glasses without modifiers.

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