Glass formation range in the SeO$_2$–TeO$_2$–V$_2$O$_5$–MoO$_3$ system

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The glass forming region in the quaternary system under increased oxygen pressure and at a slow melt cooling rate (2 to 2.5° C min^{-1}) has been determined. The stable glasses are located in the central part of the system but nearer to the SeO$_2$–TeO$_2$ side. The structural units of these two glass formers are of decisive importance in building up the glass lattice. Infrared spectra of selected compositions from the glass forming region are taken. From the data obtained for the binary glasses in the TeO$_2$–V$_2$O$_5$, TeO$_2$–SeO$_2$, TeO$_2$–MoO$_3$, V$_2$O$_5$–MoO$_3$ systems and the spectra of the four component compositions, it is shown that the basic structural units participating in the glass lattice formation are the SeO$_3$, VO$_5$, TeO$_4$ and TeO$_3$ groups. Structural models are proposed: glasses in the SeO$_2$ direction possess laminar and chain structure, while with increase of TeO$_2$ concentration, a three-dimensional structure is built up.

1. Introduction

The present work is a continuation of our investigations on the glass formation in the selenite systems [1, 2] representing a new class of amorphous materials not yet adequately examined. The aim of the work is to determine the glass formation range under increased oxygen pressure in the SeO$_2$–TeO$_2$–V$_2$O$_5$–MoO$_3$ quaternary system. Similar glasses containing SeO$_2$ can participate in the compositions of technical materials exhibiting electronic conductivity [3] or may be used for the production of ornamental glasses characterized by low melting temperatures [4], superionic conductors [5], etc.

The main difficulties in selenite glass preparation are the high volatility of SeO$_2$ and the fact that stabilization of the compositions is impossible under standard melting conditions. The submission of SeO$_2$ can be avoided by carrying out the synthesis under increased gas pressure. The glass formation in binary and ternary systems has already been investigated under such experimental conditions [1, 2]. Glasses were obtained in the following combinations: SeO$_2$–TeO$_2$, SeO$_2$–V$_2$O$_5$, SeO$_2$–MoO$_3$ [1], SeO$_2$–TeO$_2$–V$_2$O$_5$ and SeO$_2$–TeO$_2$–MoO$_3$ [2]. No glass formation was found in the TeO$_2$–V$_2$O$_5$, TeO$_2$–MoO$_3$ and V$_2$O$_5$–MoO$_3$ systems. The glass formation range in the TeO$_2$–V$_2$O$_5$–MoO$_3$ ternary system was given by Marinov et al. [6], but the data obtained by these authors were not applicable because the synthesis conditions selected in the corresponding investigations differed significantly. This is the reason for the reinvestigation of the system mentioned above.

2. Experimental details

The components were introduced to the batches as oxides (labelled for analysis). They were weighed and homogenized in a dry box, and 5 g of each were melted in quartz crucibles for 2 h under an increased oxygen pressure of $P = 35$ to 36 MPa. Autoclave equipment was used to maintain the maximal temperature for about 20 min. The samples were quenched in the digestor at a rate of 2 to 2.5° C min^{-1}. The amorphism of the samples obtained was determined visually, using the X-ray technique (Philips diffractometer) and by infrared (IR) spectra (Zeiss spectrophotometer Spenord 71-IR).

3. Results

The glass formation range obtained under increased oxygen pressure in the TeO$_2$–V$_2$O$_5$–MoO$_3$ system is represented by the hatched area of Fig. 1. The stable glasses are located in the central part. Glass formation in the quaternary system is determined in the sections parallel to the SeO$_2$–MoO$_3$–V$_2$O$_5$ triangle at 10, 20, 30, 40, 50, 60, 70 and 80 mol % TeO$_2$. It is seen that no further formation occurs at 80 mol % (Figs. 2 and 3). A three-dimensional image of the glass formation range in the quaternary system was built up (Fig. 4) from the results obtained from the ternary system and the sections.

The unshaded area in the tetrahedron represents the glass formation range while the hatched area shows the ranges of unmelted compositions, that of crystallization and of mixtures of crystals and glass. The stippled areas are the visible interior interfaces separating the compositions which can be vitrified from the rest of the spatial regions containing crystalline phases. A section which determines the glass formation range at 40 mol % is of particular interest, because, as can be seen from Fig. 4, the glass formation
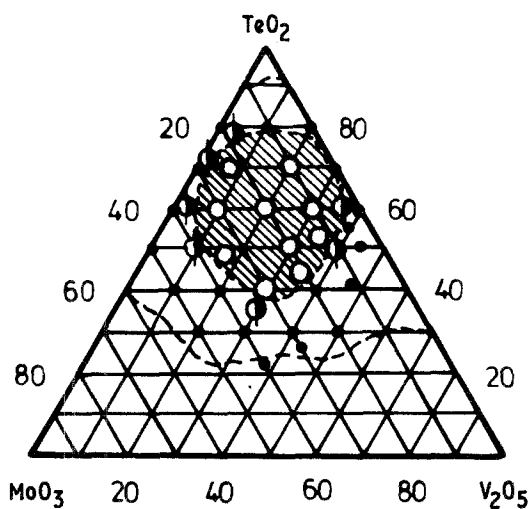
Figure 1 Glass formation range in the TeO_2–V_2O_5–MoO_3 system: O, glass; ⊙, glass and crystals; ●, crystals.

in the TeO_2–MoO_3–V_2O_5 ternary system starts in its vicinity. The most external points of the glass formation range of this section and the remaining points of the TeO_2–V_2O_5–MoO_3 line are shown by a dotted line. Thus the invisible parts of the glass formation boundaries of the SeO_2–TeO_2–MoO_3 and SeO_2–V_2O_5–MoO_3 systems are indicated. The IR spectra of the selected compositions (Table I) are shown in Figs. 5 and 6. These are typical glass spectra. Their interpretation is based on the concept of independent vibrations of individual groups of atoms [7] in the glasses. Several bands at about 1000 to 900, 850 to 860, and 700 to 640 cm^{-1} are observed.
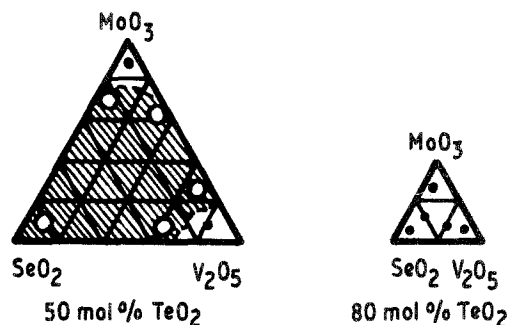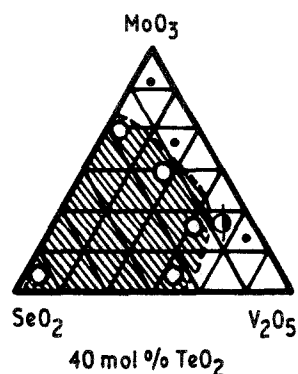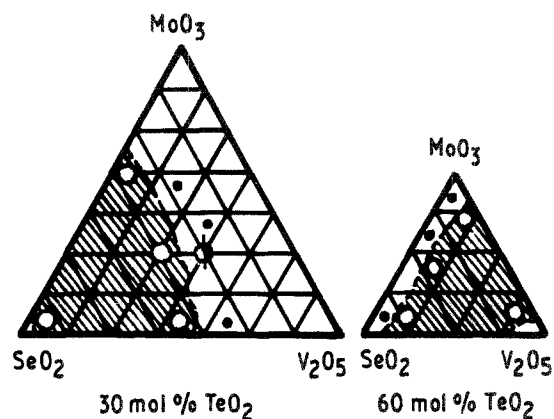

Figure 2 Glass formation ranges in the sections of the system: SeO_2–TeO_2–V_2O_5–MoO_3; with 10 and 20 mol % TeO_2.

Figure 3 Glass formation ranges in the sections of the system: SeO_2–TeO_2–V_2O_5–MoO_3; 30, 40, 50, 60, 70 and 80 mol % TeO_2.

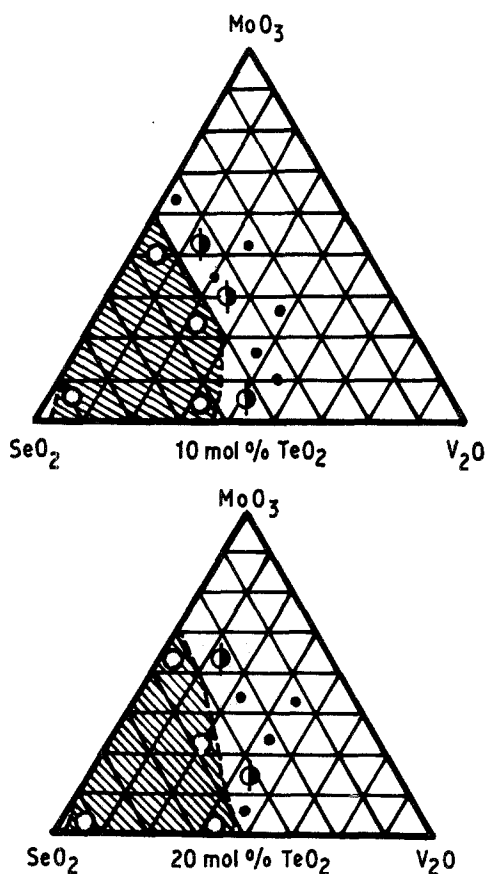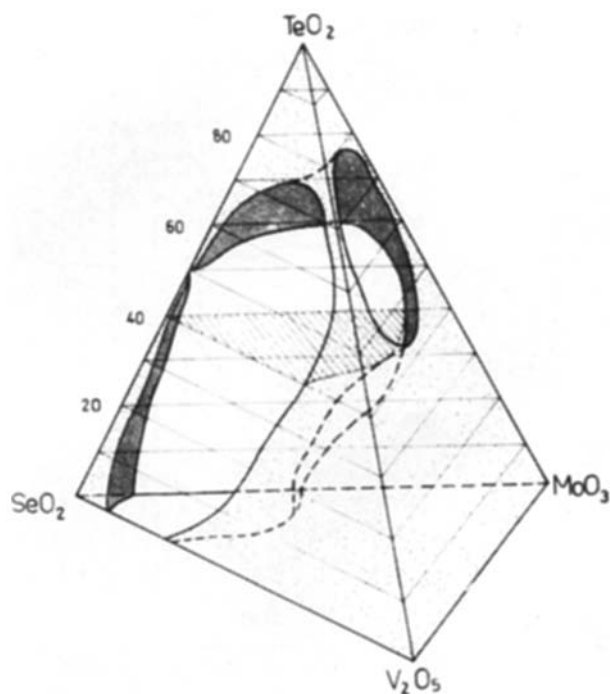*Figure 4* Spatial representation of the glass formation in the SeO_2–TeO_2–V_2O_5–MoO_3 system.

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TABLE I

Batch no.	Batch composition (mol %)	Structural units	Probable structure
1.	$60TeO_2$, $5SeO_2$, $10V_2O_5$, $25MoO_3$	TeO_4, $VO_5(VO_4)$, MoO_8	Three-dimensional
2.	$60TeO_2$, $10SeO_2$, $20V_2O_5$, $10MoO_3$	TeO_4, SeO_3, $VO_5(VO_4)$,Mo_2O_8	Three-dimensional
3.	$70TeO_2$, $15SeO_2$, $15V_2O_5$	TeO_4, SeO_3, $VO_5(VO_4)$	Three-dimensional
4.	$30TeO_2$, $20SeO_2$, $30V_2O_5$, $20MoO_3$	TeO_3, SeO_3, VO_5, Mo_2O_8	Laminated, chain
5.	$30TeO_2$, $20SeO_2$, $35V_2O_5$, $10MoO_3$	TeO_3, SeO_2, VO_5, Mo_2O_5	Laminated, chain
6.	$20TeO_2$, $35SeO_2$, $25V_2O_5$, $20MoO_3$	TeO_3, SeO_3, $VO_5Mo_2O_8$	Chain
7.	$20TeO_2$, $40SeO_2$, $45V_2O_5$, $20MoO_3$	TeO_3, SeO_3, VO_5, Mo_2O_8	Chain
8.	$20TeO_2$, $40SeO_2$, $45V_2O_5$, $20MoO_3$	TeO_3, SeO_3, VO_5, Mo_2O_8	Chain

4. Discussion

The system investigated is of great fundamental interest because it contains only structure-determining oxides which alone, or in combinations with others, build up the glass structure under definite conditions of rapid quenching.

So far it has been difficult to determine, by known structural methods, the exact structure of composite glasses such as that under investigation. However, it is possible to obtain tentative information: (a) by comparing the glass formation data (Fig. 4) with IR spectra (Figs. 5 and 6): (b) from structural information on binary glasses which constitute the quaternary systems [8–15], and (c) from structural information on known crystalline phases in it [16–22].

The basic structural units in the glasses of the TeO_2–V_2O_5 system [8–11] are TeO_4, TeO_3 and VO_5 groups, in the TeO_2–MoO_3 [12] system they are TeO_4, Mo_2O_8 and MoO_6, and as observed in the SeO_2–TeO_2 system [13, 14], the TeO_4, TeO_3 and SeO_3 groups. Glasses of the V_2O_5–MoO_3 system [15] obtained by rapid quenching have a structure derivative of that of the starting components, but not of the intermediate crystalline phase.

The results on the glass formation range (Fig. 4) show that the stable glasses are located in the central part of the system nearer to the SeO_2–TeO_2 line under the quenching conditions indicated. Hence the structural units of these two glass formers are of primary importance in the build up of the glass structure. It is possible to presume, on the basis of the conclusions made on the binary selenite–tellurite glasses [13, 14], that these would be the TeO_4 TeO_3 and SeO_3 groups (Fig. 7). In fact the band at 680 to $695\,cm^{-1}$ and the spectra of the four component glasses containing less than 50 mol % TeO_2, can be connected with vibration of TeO_3 groups [23, 24], and the shoulder at about $900\,cm^{-1}$ with the vibration of SeO_3 groups [25, 26]. The IR spectra for the SeO_2–TeO_2 binary system [14] are shown for comparison in Fig. 8. The structural units indicated can mainly participate in the formation of linear forms. Two other high-frequency bands at 1000 to 995 and $975\,cm^{-1}$ can be related to the
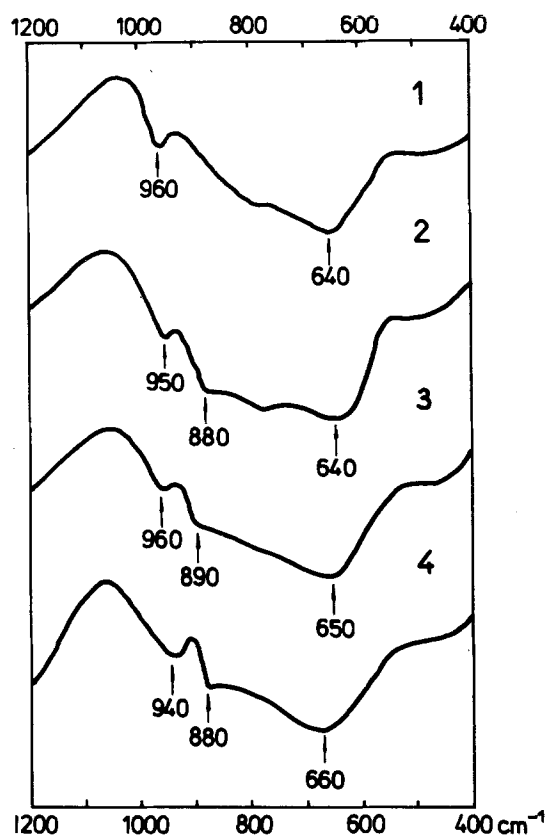
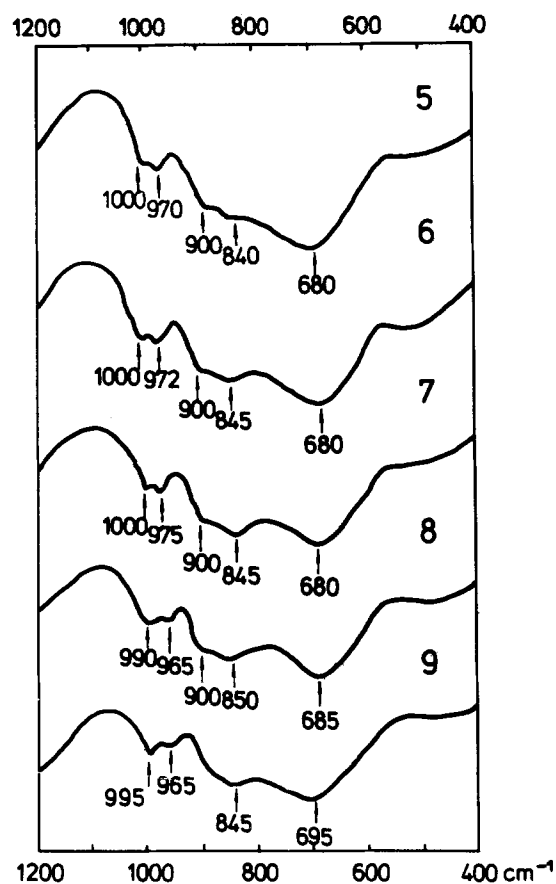Figure 5 Infrared spectra of four-component glasses containing 5 to 20 mol % SeO_2.

Figure 6 Infrared spectra of four-component glasses, containing 25 to 45 mol % SeO_2. The compositions are indicated in Table I.
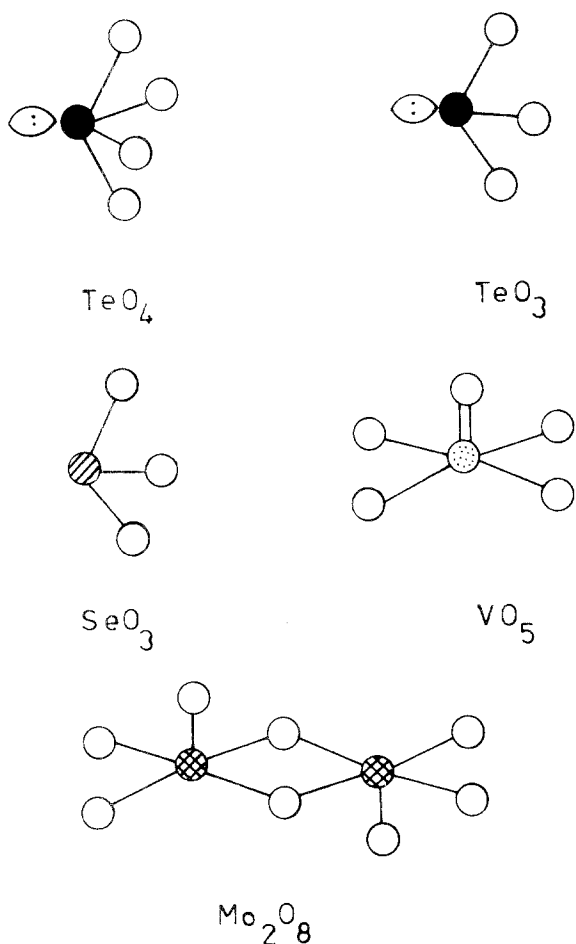
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TeO₄ ... TeO₃ ... SeO₃ ... VO₅ ... Mo₂O₈

Figure 7 Basic structural groups building up the glass lattice.

stretching vibrations of the affected and unaffected isolated $V=O$ bonds. Their appearance in the glass spectra according to Dimitriev *et al.* [27] and Sumita *et al.* [28] is a result of the presence of the VO_5 groups which take part in the build up of layers and chains. This is also verified by the presence of a band at about $840\,cm^{-1}$ which is characteristic of the vibrations of the bridging $V-O-V$ bonds. Recently, a similar inter-
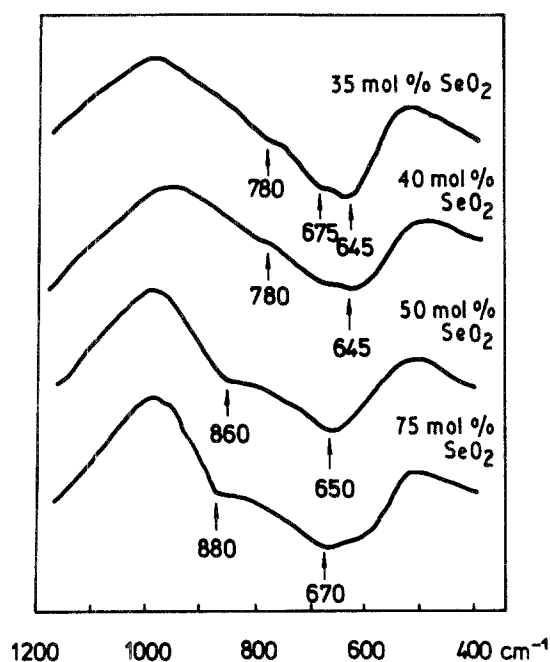

Figure 8 Infrared spectra of glasses of the binary SeO_2-TeO_2 system.

pretation of glass spectra in the $V_2O_5-B_2O_3$ system has been made [29].

It is obvious that as MoO_3 participates in limited concentration in the glasses under investigation, it does not stimulate glass formation but predominantly plays the role of a modifier. This is why it should only be included in the lattice in the form of small structural units containing isolated $M=O$ bonds. By analogy with glasses of the TeO_2-MoO_3 system [12], the band near 930 to $900\,cm^{-1}$ could be explained by the complex vibrations of Mo_2O_8.

The band at $640\,cm^{-1}(v^s_{Te-O}$ of the deformed TeO_4 groups [23, 24]) is characteristic of spectra of glasses with a high concentration of TeO_2 (Figs. 5 and 6). By analogy with the structure of binary glasses and the crystalline tellurite structure, these groups in the multicomponent glasses build up the three-dimensional lattice. In the high-frequency range only a band at about $960\,cm^{-1}$ is discovered indicating that the isolated bonds in this composition are considerably affected. It is known that the isolated bond is not directly attacked when the VO_5 groups are interconnected with groups of other glass formers [27]. Hence the frequency displacement is a result of the distribution of the electronic density with formation of $V-O-M$ instead of $V-O-V$ bonds. This can lead to a weakening and lengthening of the isolated bonds.

The formation of VO_4 groups, which is probable at low V_2O_5 concentrations, can be treated as another possiblity, in accordance with the data found for the ternary and binary compositions [30, 31]. In the latter case the frequency vibration of the isolated VO_2 groups in VO_4 polyhedra groups is about 960 to $990\,cm^{-1}$.

The absence of a tendency to liquid phase immiscibility in the whole glass formation range, which is not, in fact, observed with other combinations of TeO_2 and glass formers [32, 33], can be treated as an indirect verfication of the good compatibility of the different types of structural units. On the other hand, it is known that the free electron pair in the TeO_4 trigonal bipyramids causes deformation and diminishes their symmetry in the glasses [12]. The difficult vitrification of pure TeO_2 can be explained by their presence. This is why the good miscibility observed in the different kinds of polyhedra and the preparation of stable glasses suggest that in the selected oxide combinations the repulsive force in the area of the electron pairs is very small. The different structural polyhedra ensure spatial interconnections in a disordered lattice which is favoured energetically, and the easy realization of interchangeable bridging bonds.

5. Conclusions

The preparation of stable homogenous glasses under increased oxygen pressure and a low quenching rate is verified by experiment. Models of the structure of more complex compositions are offered by analogy with the structure of the binary glasses. It is verified that the basic structural units building up the lattice are SeO_3, VO_5, TeO_4 and TeO_3 groups. An increase in SeO_2 concentration in the glasses favours the appearance of multilayer and chain structures, while

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an increase in TeO_2 concentration favours the build up of a three-dimensional lattice.

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