JOURNAL OF MATERIALS SCIENCE 21 (1986) 3033-3037

Glass formation and immiscibility in the TeO_2–B_2O_3–Fe_2O_3–MnO system

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The glass formation in the quaternary TeO_2–B_2O_3–MnO–Fe_2O_3 system and in its ternary systems was investigated. A range of liquid immiscible phases, located near to the binary TeO_2–B_2O_3 and B_2O_3–MnO systems was established. Using transmission electron microscopy, a trend to metastable liquid-phase separation in the single-phase glasses, located near to the boundary of immiscibility was observed. With an increase in the Fe_2O_3 and MnO content still in the process of cooling of the melts, it was possible for a fine glassy crystalline structure to be formed in them. It was shown that by changing the upper limit of the melting temperature and the cooling rate, the glassy crystalline structure and the Fe_3O_4 content could be modified.

1. Introduction

Investigations on the glass formation in ternary and quaternary [1–10] systems with the participation of two glass formers, TeO_2 and B_2O_3 and oxides of Group II and Group III of the periodic table showed that it is possible to synthesize stable homogeneous glasses. Furthermore, it was established that in all the systems of the TeO_2–B_2O_3–MnO type, ranges of stable liquid-phase separation exist and in the compositions, located around them during an appropriate thermal treatment a process of metastable phase separation takes place. This process leads to the formation of a microheterogeneous structure of amorphous phases, where in accordance with electron microscopy investigations droplet-like formations predominate, but other more complicated aggregates were found, too.

The aim of the present investigation was to examine the glass formation and the immiscibility in the four-component TeO_2–B_2O_3–Fe_2O_3–MnO system. Glass formation in this system has not been investigated up to now, but data are known about some of the binary and ternary systems forming the above mentioned system. The phase diagram and the glass formation in the TeO_2–B_2O_3 system have been studied [7] and in consequence analogous results were obtained by other researchers [11]. The essential thing in this system is the formation of two immiscible liquids in a wide range of compositions above 24.5 mol % B_2O_3. In the B_2O_3–MnO system a process of stable immiscibility takes place in the range of 60 to 95% B_2O_3 [9]. It is noted also that the glass formation range depends on the extent of oxidation of the manganese ions [12]. A reaction of chemical interaction between the B_2O_3 and the MnO takes place and three congruently melting compounds were described. The eutectic temperatures were above 750° C [13]. In the TeO_2–MnO [14] and TeO_2–Fe_2O_3 [15] systems, a process of immiscibility was not found but stable glasses in relatively wide limits were obtained.

Data about the phase transformations and about the phase diagrams of the B_2O_3–Fe_2O_3 [16, 17] and MnO–Fe_2O_3 [18] systems are reported, but due to the essential influence of the oxygen on the extent of the oxidation of the transition ions, the last two systems should be considered as sections of the B–O–Fe [19] and Mn–O–Fe [18] systems. At conventional cooling rates, glasses were not obtained in these systems but the compositions possess interesting magnetic properties.

Among the three component systems forming the tetrahedron TeO_2–B_2O_3–Fe_2O_3–MnO, data are available about the glass formation in the TeO_2–B_2O_3–Fe_2O_3 and TeO_2–B_2O_3–Fe_2O_3 [9] systems and partially about the B_2O_3–MnO–Fe_2O_3 [20, 21] system. The investigations in the present work were directed towards the examination of the glass forming ability in the three component systems: TeO_2–MnO–Fe_2O_3, TeO_2–B_2O_3–Fe_2O_3, Fe_2O_3–MnO–B_2O_3 and sections of four component systems as well, on which to build up the basis of the spatial image of the glass forming region and the immiscibility in the quaternary system.

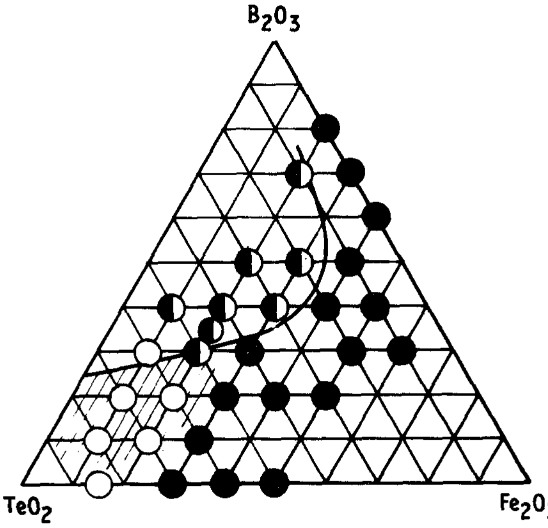


Figure 1 Glass forming region in the TeO_2–B_2O_3–Fe_2O_3 system: (○) glass, (●) crystallization, (◑) liquid–liquid phase separation.

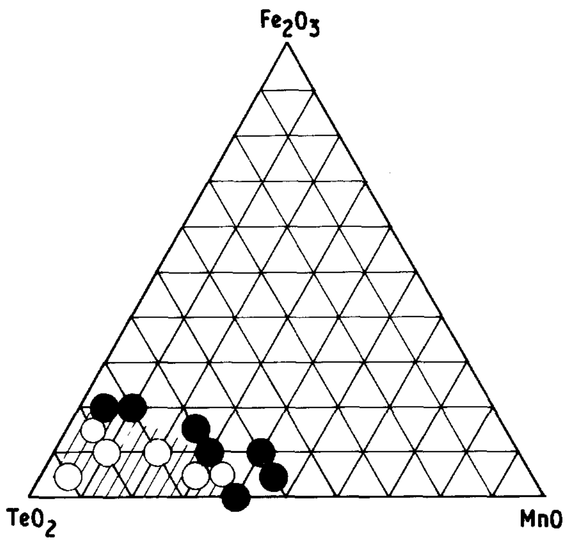


Figure 2 Glass forming region in the TeO_2–Fe_2O_3–MnO system.

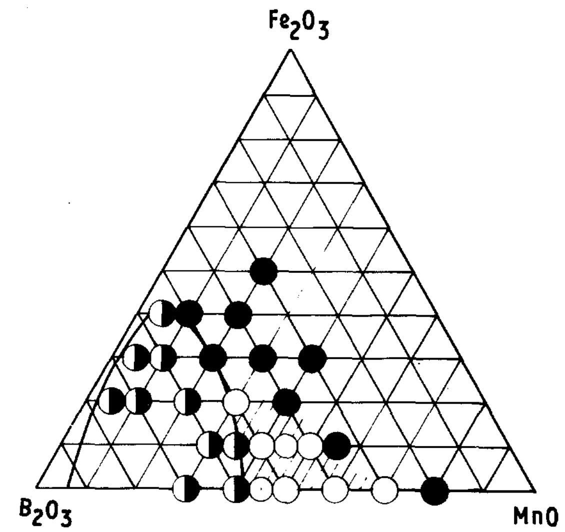


Figure 3 Glass forming region in the B_2O_3–Fe_2O_3–MnO system.

2. Experimental details

As starting materials for the preparation of the compositions TeO_2, H_3BO_3, Fe_2O_3, and MnO_2 (labelled for analysis) were used. The melting was performed in an electrical furnace at a temperature of 800 to 1000° C in porcelain or corundum crucibles depending on the melting temperatures of the batch in a quantity about 10 g. The quenching was performed in the crucibles at a rate of 100° C min^{-1}, giving a possibility of processes of microphase and macrophase separation taking place. In some cases in order to fix the glassy state the cooling rate was increased to about 1000° C min^{-1} by pouring the melt over a metal surface. For the preparation of thin bands in the glassy state of compositions possessing high crystallization ability, or to prevent a trend to microphase separation, a roller technique for rapid quenching of the specimens was used. The cooling rate in the apparatus exceeded 10^5 ° C sec^{-1}.

The phase and structural investigations were carried out by using a Philips electron microscope, X-ray diffractometer URS 50 IM and Paulik–Paulik derivatograph.

3. Results and discussion

In Fig. 1 data about the glass forming regions and liquid phase separation in the TeO_2–B_2O_3–Fe_2O_3 system are presented.

In contrast to the small glass forming region, the immiscibility covers much greater compositions. For some of them, located close to the boundary of stable immiscibility, a trend to metastable liquid phase separation was observed. With increasing Fe_2O_3 concentration, the compositions become more heat resistant.

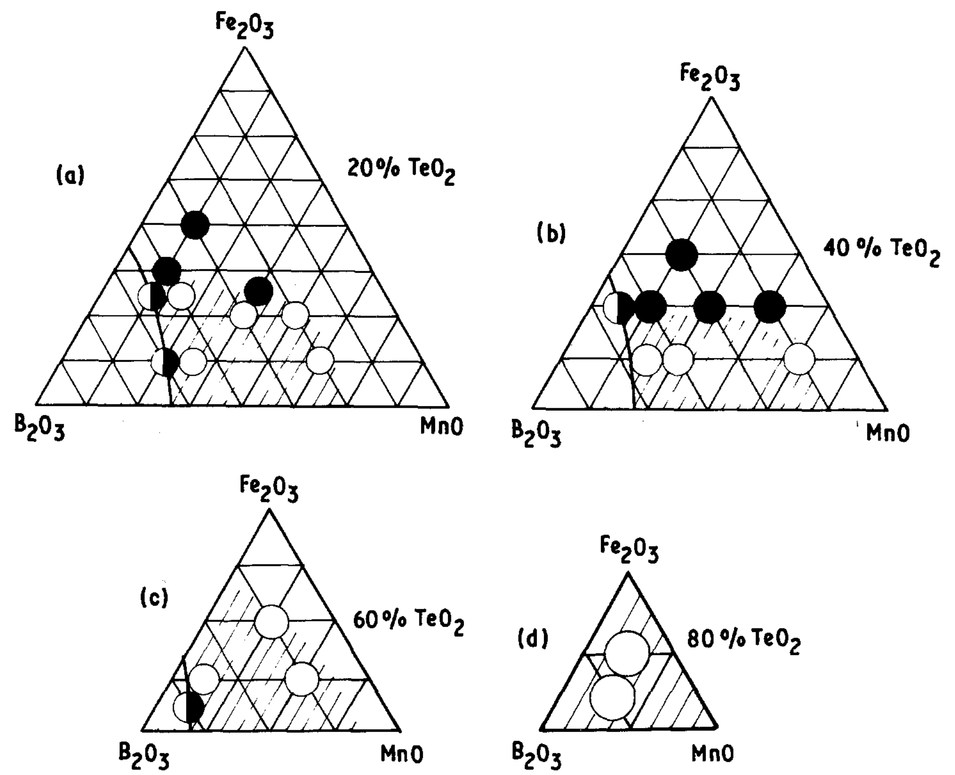


Figure 4 Glass forming region and sections of the TeO_2–B_2O_3–MnO–Fe_2O_3 system. (a) at 20% TeO_2, (b) 40% TeO_2, (c) 60% TeO_2 and (d) 80% TeO_2.

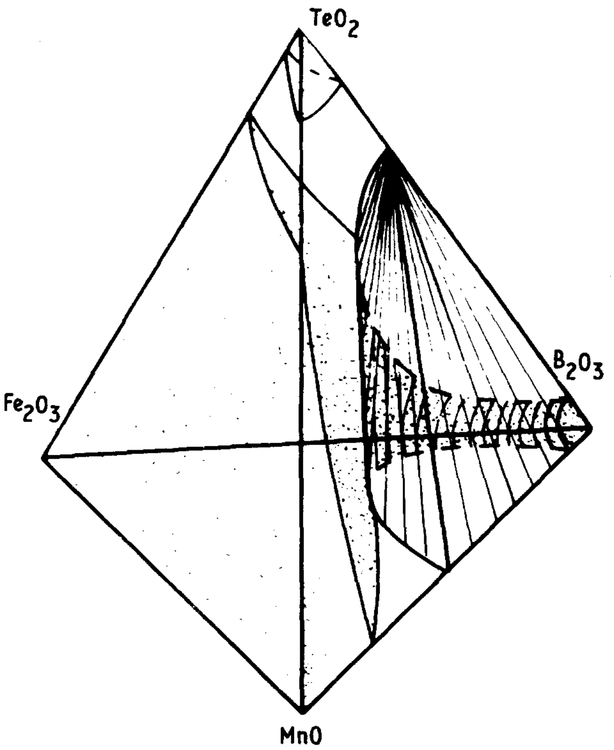


Figure 5 Spatial image of the glass forming region in the TeO_2–B_2O_3–MnO–Fe_2O_3 system.

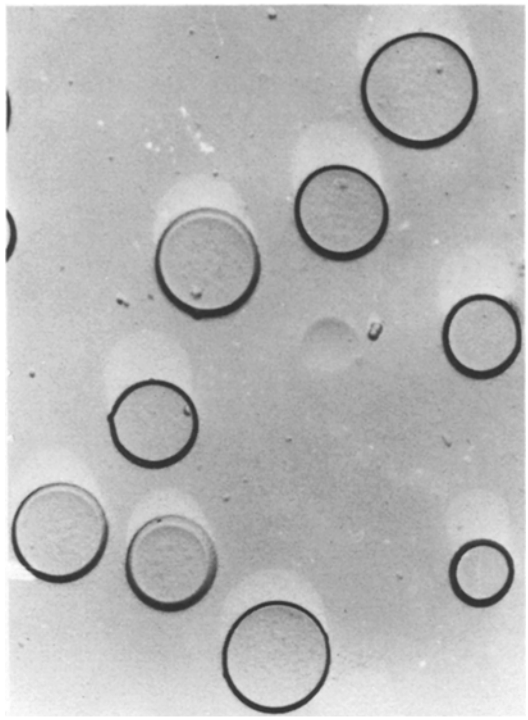
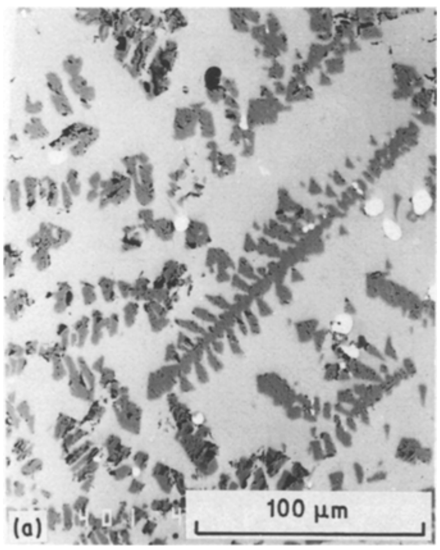


Figure 6 Metastable phase separation in supercooled melt to glassy state. Composition 45 B_2O_3 · 10 Fe_2O_3 · 45 MnO, (TEM × 6000).

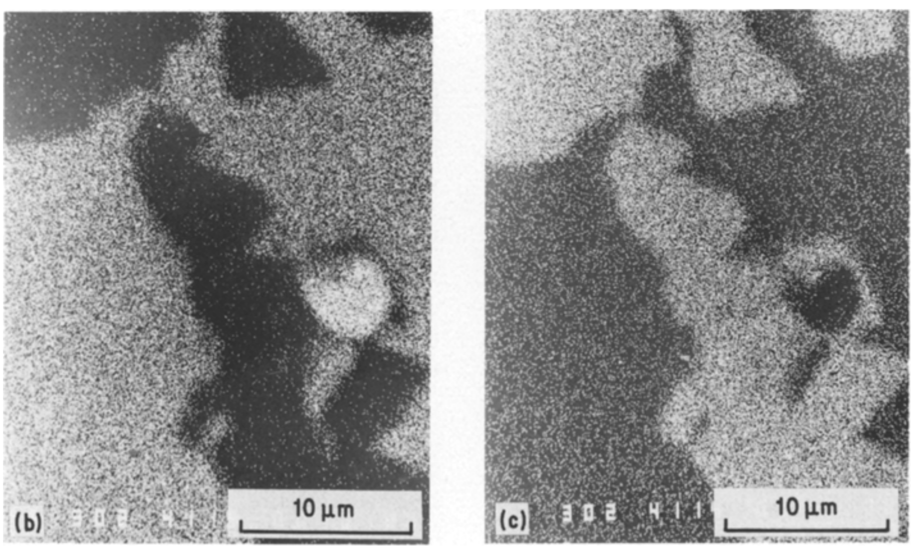


In spite of that, some of the specimens could be separated visually into two layers, in fact this is due to the process of melting.

The crystallization temperature T_K, in accordance with the data from differential thermal analysis (DTA) varies from 500 to 550° C. On the diffractograms of the compositions in the direction of TeO_2 to Fe_2O_3 the following crystalline phases were identified: TeO_2, 4 $TeO_2Fe_2O_3$, $TeO_2Fe_2O_3$ and Fe_2O_3.

The glass forming region in the TeO_2–Fe_2O_3–MnO system (Fig. 2) is also small and it is located near to TeO_2. No immiscibility was observed. The crystallization of the compositions located around the glass

Figure 7 Dendrite crystallization in a rapidly quenched specimen with composition 30 TeO_2 · 20 B_2O_3 · 10 MnO · 40 Fe_2O (a) Compo × 400, (b) analysis on points Te $L\alpha$ (c) Fe $K\alpha$.



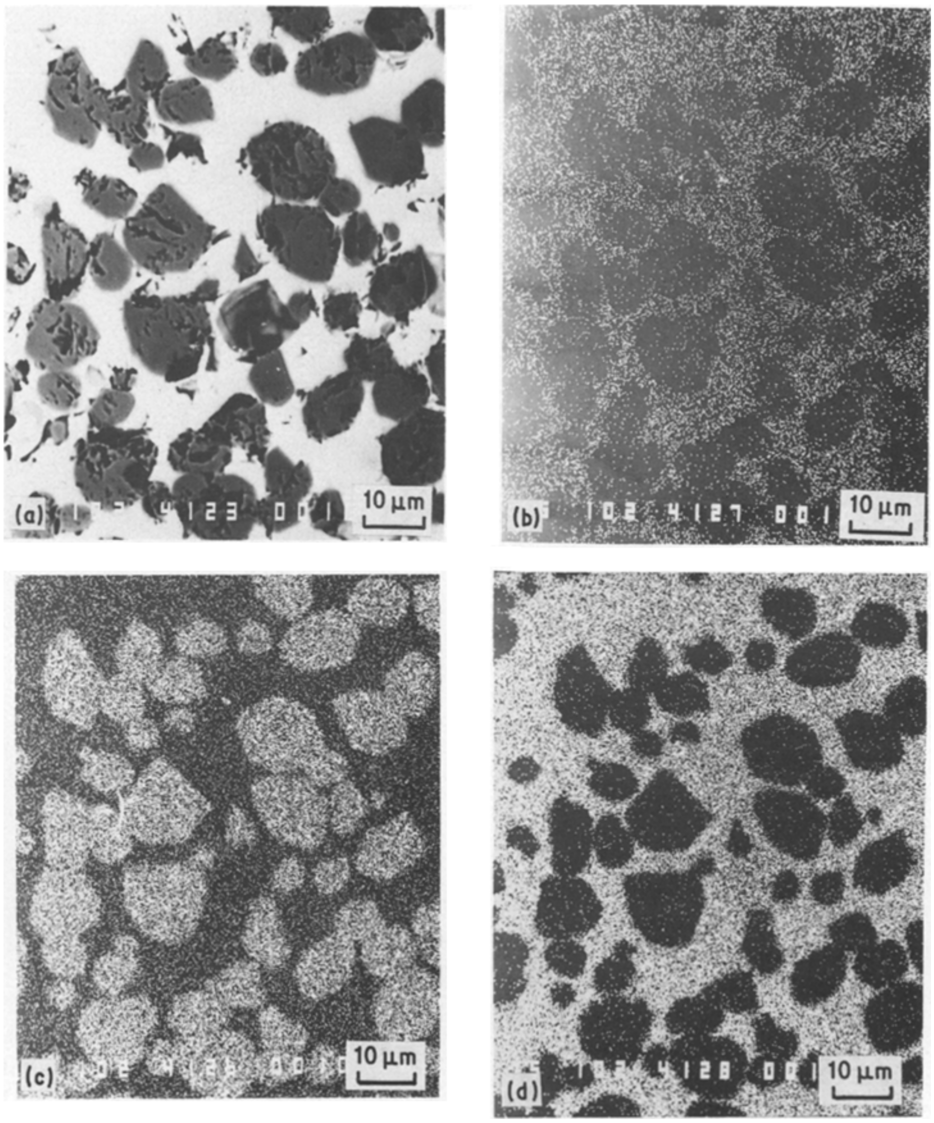


Figure 8 Formation of plate crystals in a slowly cooled specimen with composition 30 $TeO_2 \cdot 20\ B_2O_3 \cdot 10\ MnO \cdot 40\ Fe_2O_3$, melted at 1300° C (a) Compo × 1000, (b) analysis on points Mn $K\alpha$, (c) Fe $K\alpha$ and (d) Te $L\alpha$.

formation boundary takes place in bulk, and a fine crystalline structure was formed.

In the B_2O_3–MnO–Fe_2O_3 system (Fig. 3) stable liquid phase separation in the compositions, located around B_2O_3 was observed. The lower layer is black in colour and mainly Fe_2O_3 crystallizes in it, the upper layer is opaque white glass with a high percentage of B_2O_3, which hydrates in air. Glasses are black in colour, without glass brightness, strongly darkened. The melts are very aggressive towards the porcelain crucibles, therefore the melting was carried out in a corundum crucible. The crystallization temperature according to the data from the DTA is 800 to 850° C. The compositions located around the glass forming region possess a fine crystalline structure. The X-ray phase analysis of these compositions showed that crystalline phases are separated: Fe_3O_4 and MnO · Fe_2O_3, and some of them possess ferromagnetic properties.

Glass formation in the quaternary combination TeO_2–B_2O_3–Fe_2O_3–MnO is investigated in 4 sections, corresponding to 20, 40, 60 and 80 mol % TeO_2 (Fig. 4). The spatial image of the glass formation and the stable immiscibility is shown in Fig. 5. It is seen that the immiscibility compositions cover the range close to the B_2O_3. As in the previous systems, a process of metastable liquid phase separation of droplet-like type in the compositions outside the boundaries of stable immiscibility (Fig. 6) was observed.

The glass forming region is relatively narrow in the base of the tetrahedron (Fig. 5). The stable glasses are located mainly around the axis connecting the TeO_2 with one central composition: 50 $B_2O_3 \cdot 20\ Fe_2O_3$ 30 MnO of the B_2O_3–MnO system. The four component composition rich in Fe_2O_3 and MnO crystallizes easily and a fine glassy crystalline structure is formed during the cooling of the melts. Compositions containing above 40 mol % Fe_2O_3/Fe_2O_3 (Fe_2O_3 + MnO 50 mol %) possess magnetic properties [22]. Since the quantity of the crystals in the total mass is very small, their identification is difficult. Interplanar distances for Fe_3O_4 (d = 0.253, 0.209, 0.16 and 0.148 nm) and Fe_2O_3 (d = 0.269 and 0.170 nm) were recorded, using an X-ray technique.

Changing the initial temperature of melting and the cooling rate of the melts, it was established that the magnetic properties could vary in wide ranges. It is assumed that the increase in the upper temperature of melting changes the Fe_3O_4 content, about which is known that, it is produced by thermal dissociation of the Fe_2O_3 above 1300° C [23, 24]. In fact, in accordance with electron microscopy observations the specimens quenched at the higher temperature contain crystalline dendrites with a high iron concentration (Fig. 7), even elemental tellurium. X-ray phase analysis showed that the iron present is mainly as Fe_3O_4 crystals. After repeated thermal treatment in the 500 to 700° C range, Fe_2O_3 was formed, and as a result the magnetic permittivity reduces sharply. The morphology of the crystals in slowly quenched specimens is also specific: well defined crystals of about 10 μm were formed (Fig. 8).

4. Conclusions

The glass formation ranges and those of the liquid–liquid phase separation in the TeO_2–B_2O_3– Fe_2O_3–MnO system are determined. Using electron microscopy techniques a metastable liquid phase separation of a droplet-like type was established in compositions located around the boundaries of stable liquid phase separation. Glass crystalline materials were synthesized from compositions located near to the boundary of glass formation during the process of quenching of the melts. It was shown that the variation in the magnetic permittivity in these samples is due to the change of the ratio between Fe_3O_4 and Fe_2O_3.

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Received 15 August
and accepted 30 October 1985