LIQUID PHASE SEPARATION IN THE SYSTEMS TeO_2-B_2O_3-M_2O_3 (M_2O_3 = Al_2O_3, Ga_2O_3, Sc_2O_3, La_2O_3, Bi_2O_3)

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Liquid phase separation was studied in three component systems TeO_2-B_2O_3-M_2O_3, where M_2O_3 = Al_2O_3, Ga_2O_3, Sc_2O_3, La_2O_3 and Bi_2O_3. The boundaries between one- and two-phase glasses were determined. Near these boundaries different cases of microheterogeneous structure as a result of metastable immiscibility were established by transmission electron microscopy (TEM). IR data analysis indicated that the existence of homogeneous glasses is related with the simultaneous participation of BO_3- and BO_4-groups in the glassy network.

Keywords: TeO_2 glasses, Immiscibility, Microstructure

INTRODUCTION

The tellurite glasses are important non-traditional amorphous materials due to their possible applications in the optics and optoelectronics [1, 2]. The knowledge of the structure and properties of these glasses contributes to their successful use. The aim of the present work is to study the glass-formation and liquid phase separation in tellurite-borate systems containing as a third component one of the following oxides: Al_2O_3, Ga_2O_3, Sc_2O_3, La_2O_3 and Bi_2O_3. This investigation is a continuation of our previous studies concerning the microstructure of three component tellurite-borate glasses [3, 4].

EXPERIMENTAL PART

The samples were obtained by traditional melting technology using alumina crucibles. The slow cooling of the melts using a rate of 100 °C/min was applied. The high melting temperatures of the third components limit the number of investigated compositions as the evaporation of the TeO_2 is significant above 1200 °C. The samples were characterized by their nominal compositions.

Transmission electron microscopy (TEM) investigations were made on all obtained glasses using EM-400, Philips by replica technique from fresh fractured and chemically treated (2 vol.% HF acid for 10 s) surfaces of bulk samples. In order to distinguish the main structural units in the glassy networks infrared spectra (from 2000 to 400 cm^{-1}) in KBr disks of the samples were measured using FTIR-spectrometer Bruker EQUINOX 55.

RESULTS AND DISCUSSION

The glass-formation regions in all systems investigated are relatively narrow: in the TeO_2-B_2O_3-Ga_2O_3 and TeO_2-B_2O_3-Sc_2O_3 systems, they are located near the TeO_2 side (figure 1). In the other systems, monophase glasses are synthesised also from some compositions in the central part of Gibbs triangles: up to 20 mol.% Al_2O_3, 25 mol.% La_2O_3 and 50 mol.% Bi_2O_3 where the largest glass-forming region is found.

Stable liquid-liquid phase separation exists in all systems studied for compositions situated close to the TeO_2-B_2O_3 side. For the systems containing Sc_2O_3, La_2O_3 and Bi_2O_3 the boundaries between one- and two-phase glass regions continue towards the side of the binary B_2O_3-M_2O_3 systems (see figure 1). In compositions near the stable phase separation regions, metastable immiscibility microstructures having form of droplet-like formations or more complex aggregates dispersed in amorphous matrix were observed. Figure 2 shows an example of such microstructure for one-phase glass from the system containing Bi_2O_3. Immiscibility droplets are found also in both layers of two-phase glasses. In the system TeO_2-B_2O_3-Ga_2O_3 some of them having size between 0.1 μm and 0.5 μm are enriched in B_2O_3 . This corresponds with their higher corrosion ability (figure 3). For all systems with elevated amount of the third component, the crystallization ability is achieved and microcrystals distributed in an amorphous matrix are found. This trend is strongly developed in compositions containing Al_2O_3 (figure 4).

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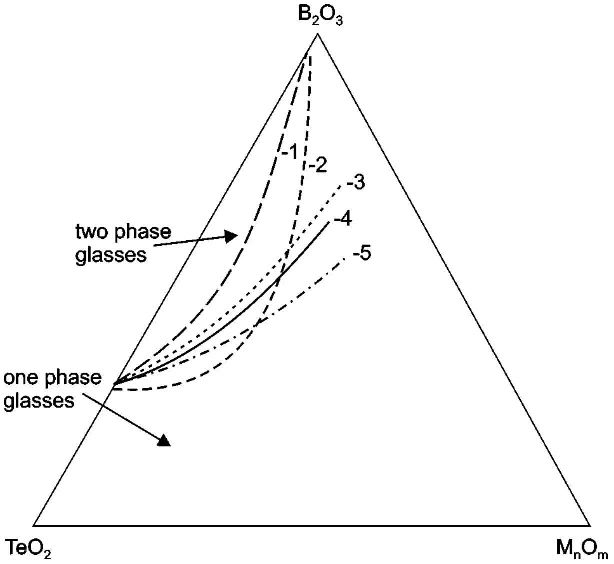

Figure 1. Boundaries between one- and two-phase glass regions in the systems TeO_2-B_2O_3-M_2O_3: M_2O_3= (1) Al_2O_3; (2) Ga_2O_3; (3) Sc_2O_3; (4) La_2O_3; (5) Bi_2O_3.

The results of TEM observations show the influence of the third component on the immiscibility tendency in different tellurite-borate glasses. In our previous works [5 - 8], the pronounced trend for cluster formation in slowly cooled pure vitreous B_2O_3 (v-B_2O_3) has been discussed. The presence of nano-scale heterogeneities in v-B_2O_3 ranging in sizes between 1.5 - 2 nm was experimentally established by TEM data [6, 7]. According to the classification of Zarzycki [9] and Porai-Koshits [10], they were associated with the thermal density fluctuations. By means of MM computer simulation, we made an attempt to model the cluster formation in borate network at the presence of BO_3-groups and B_3O_6-boroxol rings [5, 7, 8]. The addition of TeO_2, containing mainly TeO_3-groups, stimulates the clustering at micro-scale level [5, 7] and leads to appearance of metastable phase separation. In this sense, the role of the third component should be assigned to its influence on the formation of different borate or tellurite complexes.

Some typical IR-spectra of chosen compositions in binary and three component systems are shown in figures 5 and 6. Their interpretation is based on IR data analysis of borate glasses [11 - 15]. According to the obtained IR-spectra the B_2O_3 participates as BO_3- (1380 and 1240 cm^{-1}) and BO_4-groups (900 cm^{-1}) in the network of the binary tellurite glass, in spite the small B_2O_3 amount in the composition (figure 5 - 1). Similar spectra are obtained when La_2O_3 is added to TeO_2-B_2O_3 glass, but the intensity of the band at 1325 cm^{-1} increases at the expense of the band at 1215 cm^{-1}, leading to an increase in the tendency for formation of superstructural units containing BO_3- and BO_4-groups (figure 5 - 2). This trend is developed (1380, 1050 and 940 cm^{-1}) for composition with higher B_2O_3 content

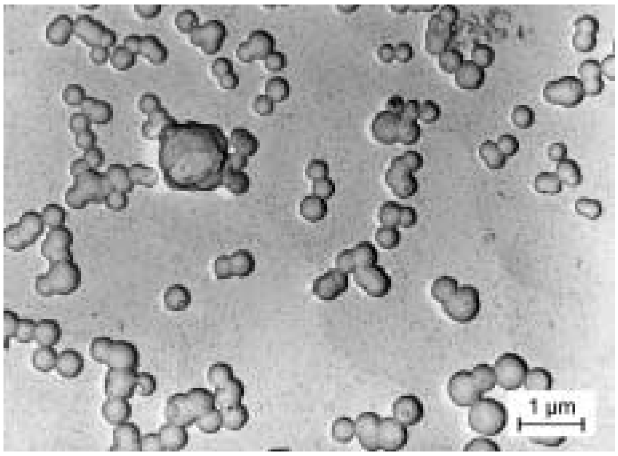

Figure 2. Immiscibility droplets and micro-aggregates in one-phase glass with composition $70TeO_2$,$20B_2O_3$,$10Bi_2O_3$ (mol.%).

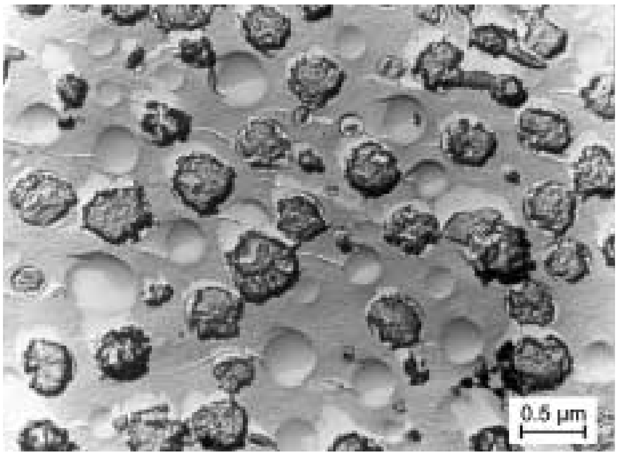

Figure 3. B_2O_3-enriched immiscibility droplets in the low layer of two-phase glass with composition $20TeO_2$,$70B_2O_3$,10 Ga_2O_3 (mol.%).

Figure 4. Microcrystals dispersed in amorphous matrix of glass with composition $50TeO_2$,$30B_2O_3$,$20Al_2O_3$ (mol.%).

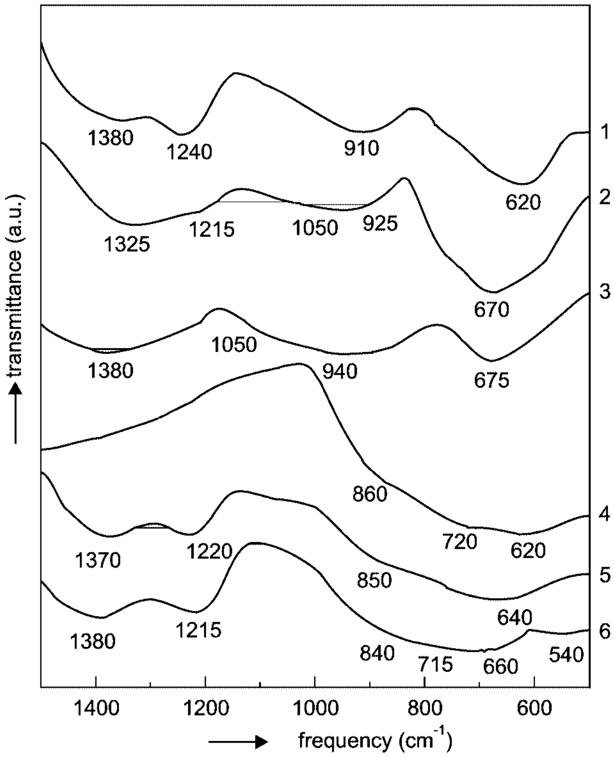

Figure 5. IR-spectra of glasses with compositions (mol.%): (1) - $74TeO_2$, $26B_2O_3$; (2) - $60TeO_2$, $20B_2O_3$, $20La_2O_3$; (3) - $20TeO_2$, $60B_2O_3$, $20La_2O_3$; (4) - $85TeO_2$, $15Al_2O_3$; (5) -$80TeO_2$, $10B_2O_3$, $10Al_2O_3$; (6) - $60TeO_2$, $20B_2O_3$, $20Al_2O_3$.

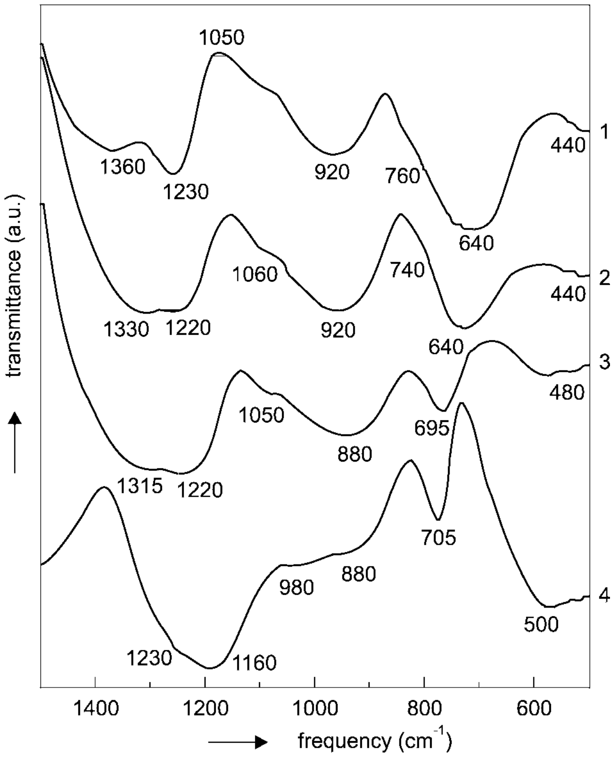

Figure 6. IR-spectra of glasses with compositions (mol.%): (1) - $60TeO_2$, $30B_2O_3$, $10Bi_2O_3$; (2) - $30TeO_2$, $40B_2O_3$, $30Bi_2O_3$; (3) - $50B_2O_3$, $25Bi_2O_3$, 25PbO; (4) - $25B_2O_3$, $50Bi_2O_3$, 25PbO.

(60 mol.%) and lower TeO_2 content (figure 5 - 3). The same situation is observed in the spectra of the three component glasses containing Bi_2O_3 (figure 6 - 1, 2). In these one-phase glasses, the trend of the formation of BO_4-units in the network (bands near 900 - 1000 cm^{-1}) increases. The appearance of BiO_6-groups is proved by the band near 480 cm^{-1}. The spectra of two three-component bismuthate glasses without TeO_2 (figure 6 - 3, 4) are shown for comparison.

The replacement of the La_2O_3 by Al_2O_3 leads to differences in the IR-spectra (figure 5 - 5, 6). The bands at 1380 and 1215 cm^{-1} appear with increased intensity, while the bands at about 1000 and 900 cm^{-1}, assigned to the BO_4-groups, disappear. Probably isolated BO_3-triangles or more complex units with their participation are formed.

The vibrations at about 640 cm^{-1} are characteristic for tellurite glasses containing TeO_4-groups. Their displacement towards lower frequencies is connected with some additional deformation of TeO_4-groups due to the appearance of more complicated tellurite units [16, 17]. The opposite displacement of this band towards higher frequencies (660 - 680 cm^{-1}) is connected with the increasing number of the TeO_3-groups [18]. Depending on the composition, both tendencies are observed in the obtained IR-spectra.

The role of the borate units in the network for determination of the liquid phase separation boundaries has been discussed recently by Tomozawa [19], especially in connection with their changes with the temperature. In our case, we made an attempt to use the IR-spectral data to explain the correlation between the glassy network building, the formation of nano-scale clusters and their further structural evolution towards different immiscibility structures. As it was discussed, the tendency of cluster formation is typical for the borate network containing boroxol rings [5,7,8]. According to the IR-spectra these structural units are not presented in the investigated three component one-phase glasses which compositions are beyond the immiscibility regions. Based on these results it is possible to develop a hypothesis for the reasons stimulating the tendency for liquid phase separation in B_2O_3-containing glasses. The formation in the glassy network of superstructural units containing simultaneously BO_3- and BO_4-groups is probably the reason for the depressing tendency to immiscibility, because in this case only strong bridging bonds are formed in the network.

CONCLUSION

The boundaries between one- and two-phase glasses were determined in three component systems TeO_2-B_2O_3-M_2O_3, where M_2O_3 = Al_2O_3, Ga_2O_3, Sc_2O_3, La_2O_3 or Bi_2O_3. Near these boundaries metastable droplet-like immiscibility microformations were established. The decrease amount of the boroxol units and the increasing of the superstructural units, containing simultaneously BO_3- and BO_4-groups, improved the formation of the glassy network and thus stimulated the existence of homogeneous glasses.

Acknowledgement

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FÁZOVÁ SEPARACE V SYSTÉMECH TeO_2-B_2O_3-M_2O_3 (M_2O_3 = Al_2O_3, Ga_2O_3, Sc_2O_3, La_2O_3, Bi_2O_3)

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V trojsložkových systémech byla studována fázová separace TeO_2-B_2O_3-M_2O_3 (M_2O_3 = Al_2O_3, Ga_2O_3, Sc_2O_3, La_2O_3, Bi_2O_3). Byla určena rozhraní mezi jedno a dvojsložkovými skly. V blízkosti těchto rozhraní byla transmisní elektronovou mikroskopií nalezena mikro-heterogenní struktura jako výsledek metastabilního odmísení. Analýza infračervených spekter ukázala, že existence homogenních skel je ovlivněna simultánní účastí BO_3- a BO_4-skupin ve skelné struktuře.