JOURNAL OF MATERIALS SCIENCE 10 (1975) 1419–1424

Immiscibility in the TeO_2–B_2O_3 system

Y. DIMITRIEV, E. KASHCHIEVA
Higher Institute of Chemical Technology, Darvenitsa, Sofia-56, Bulgaria

Experimental investigations have been carried out to study the phase separation process in the TeO_2–B_2O_3 system. It was found that the phase diagram is of a eutectic-like type (monotectic invariant reaction), with a wide region of stable and metastable phase separation. During the cooling of the melts two phases are obtained. One has a high TeO_2 content and is a transparent glass. The other, richer in B_2O_3, is opaque and in structure constitutes a complicated microheterogeneous system.

1. Introduction

It is well-known that the addition of certain alkaline earth oxides to a number of binary systems in the presence of B_2O_3 or SiO_2 glass formers leads to the formation of wide immiscibility regions [1]. On their part alkali oxides, especially Li_2O and Na_2O, only promote the appearance of metastable phase separation [2, 3]. It is also known that tellurium dioxide, which may also be classed with the glass formers, forms, under interaction with these oxides, a phase diagram with no immiscibility regions, and mainly with congruently melting compounds [4-6]. It would be of interest to follow up the processes of miscibility in a B_2O_3 (or SiO_2) and TeO_2 compound as a model system, since such a compound would probably favour the formation of a homogeneous melt, whereas B_2O_3 would act in the reverse direction.

Our initial investigations [7] of the TeO_2–B_2O_3 system, as a part of the TeO_2–B_2O_3–V_2O_5 three-component glass forming system, indicated that glass-formation in it is possible. The trend towards phase separation, however, was not examined in [7]. Subsequently, this trend was found to be one of the causes of the unsatisfactory reproducibility of the boundaries of the glass-forming region. This prompted us to conduct a study of the immiscibility in the TeO_2–B_2O_3 system.

2. Method of investigation

The experiments were carried out with H_3BO_3 and TeO_2 (labelled "for analysis, USSR"). Batches, each for 10 g of melt, were prepared. Melting was performed in quartz crucibles in a kanthal furnace at a temperature of 800 to 920° C; the temperature was held at the maximum for about 15 min. The melts obtained in this manner were allowed to cool in the crucibles and, after a visual appraisal of the phase separation, electron microscopic examinations were undertaken. All observations were, therefore, carried out on samples obtained under non-equilibrium conditions*. The freshly fractured surfaces of the samples were etched with 2% hydrofluoric acid solution for 10 sec, after which carbon-platinum replicas were prepared from them†. The appropriate acid concentration and the duration of etching were determined by carrying out a series of experiments, which are of a certain methodical interest, not within the scope of this work.

We would like to note here that whilst the acid treatment led to a better development of the droplets, it could also lead to a considerable etching and deformation. At the same time, a general corrosion of the basic matrix on a larger scale was observed. This may be seen from Figs. 1 and 2 where the coarse-grained spheroidal formations overlapping each other are due to the matrix corrosion; only the smaller droplets which are corroded inside, and are randomly dispersed on the larger ones have a character of metastable phase separation. It should be noted that this corrosion of the matrix cannot be related

---

* Our studies on phase separation, by controlling the rate of cooling, as well as the results after treatment at different temperatures, will be published separately.

† The observations were made with a Zeiss ELMI-D2 electron microscope and with a JEOL JSM-S1 scanning electron microscope.

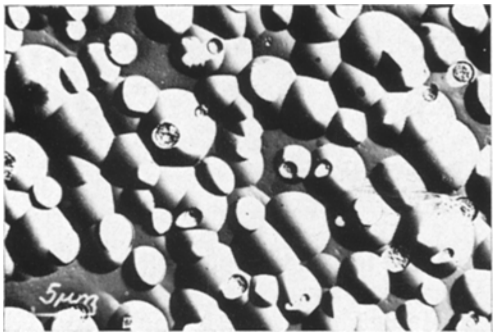

Figure 1 Replica electron micrograph of the clear phase of a $65TeO_2$, $35B_2O_3$ sample etched for 10 sec with a 10% hydrofluoric acid solution, × 1500.

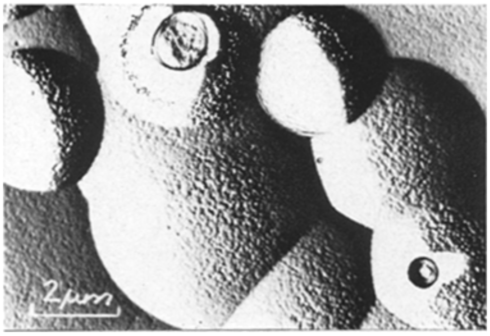

Figure 2 Replica electron micrograph of another region of the same sample as in Fig. 1. The larger magnification (× 4500) enables the general corrosion of the surface to be seen more clearly.

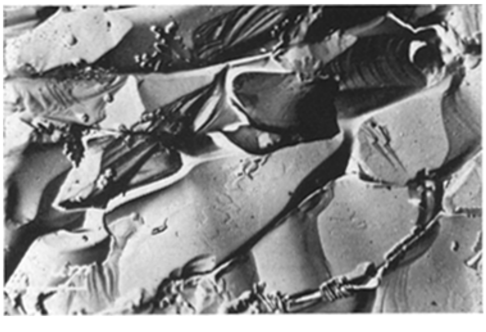

Figure 3 Replica electron micrograph of a $95TeO_2$, $5B_2O_3$ sample crystallized in the course of pouring the melts on to a copper surface, × 1500.

to the microheterogeneous structure of the glasses observed by us.

Tellurium distribution in the matrix and in several droplets of a suitable size, was investigated with the aid of X-ray microanalysis, using a Hitachi XMA-5.

Finally, untreated, as well as heat-treated samples were subjected to electron diffraction investigation with a Zeiss EF-6 electron microscope and to X-ray phase analysis with an URS 50 IM X-ray diffractometer, with Cu$K\alpha$ radiation and a nickel filter.

3. Experimental results

The results obtained from the experiments indicate that the samples rich in TeO_2 possess a high crystallization ability (Fig. 3). In the batch composition below 94 to 95 mol % TeO_2, however, it is possible to fix a glassy state. By means of a certain modification in the conditions for synthesis, the glass-formation boundary may be shifted down by a further 10 to 15 mol % TeO_2. Visually, the samples are clear and yellow-green in colour. If the cooling rate is changed, it is also possible to obtain opaque glasses of a greenish tinge. As is seen in Fig. 4a to d, their structure is microheterogeneous. The spherical formations observed, from 0.05 (Fig. 4a) to 4 to 5 μm (Fig. 4d) in size, are scattered in the amorphous matrix which is also not completely homogeneous. Fine droplets (background structure), retaining their size and concentration, even when varying the batch composition, are detected in it.

The fine-grained inner structure of the largest droplets in a sample of 85 % TeO_2 is illustrated in Fig. 5. Owing to acid treatment, the corrosion process advances to such a degree as to make it possible to see that each of these large droplets possess a well-shaped envelope (Fig. 6) similar to those first observed by Vogel in the $BaO–B_2O_3–SiO_2$ system [8]. The tearing in the course of cooling leads to an "outflow" of the fine grains in the droplets towards the matrix bulk (Fig. 7).

Below 74.5 mol % TeO_2 (sample analysis), a liquid–liquid phase separation takes place, resulting in two completely immiscible liquids. The lower layer, referred to below as the first phase, is a typical glass of yellowish-green colour, whereas the upper layer, named the second phase, is opaque and milk-white. A further increase in the B_2O_3 concentration alters the quantitative correlation between the two layers. The second phase grows in volume and, at a composition of $\sim$ 8 mol % of B_2O_3, the clear glass disappears visually. It may be detected in several compositions only as individual drops,

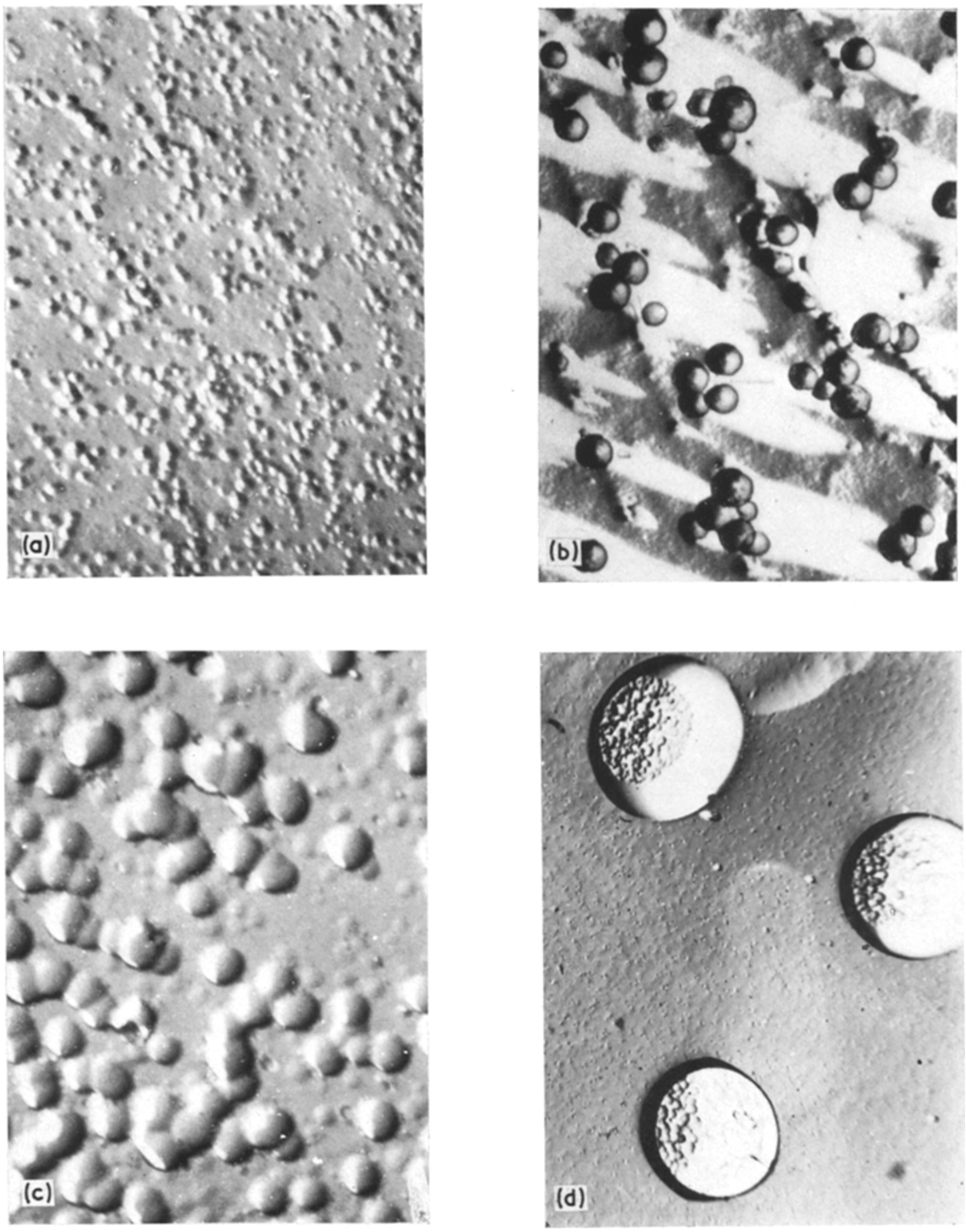

Figure 4 Replica electron micrographs of samples illustrating the size enlargement of the spherical formations solely due to the decrease of the TeO_2 content from (a) to (d). (a) $96.5TeO_2$, $3.5B_2O_3$ sample; × 18 000. (b) $94.3TeO_2$, $5.7B_2O_3$ sample; × 18 000. (c) $88TeO_2$, $12B_2O_3$ sample; × 18 000. (d) $85TeO_2$, $15B_2O_3$ sample; × 4500.

ranging in diameter from 1 μm to 1 mm (Fig. 8). The X-ray microanalysis provides evidence that these drops are a TeO_2-rich phase. The X-ray image of one of these drops is presented in Fig. 9 (the micro-regions having a higher distribution density of light points whch correspond to

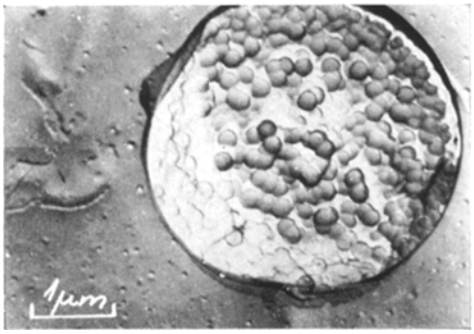

Figure 5 Replica electron micrograph of a droplet with a fine-grained inner structure of composition $85TeO_2$, $15B_2O_3$, × 9000.

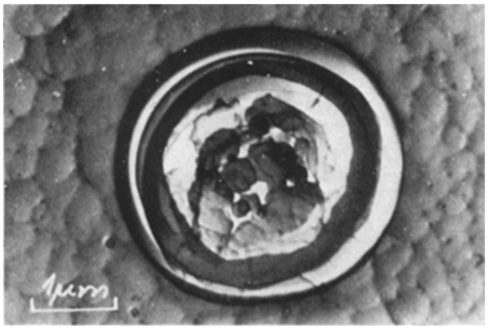

Figure 6 Replica electron micrograph of a droplet with a well-shaped envelope of the intermediate phase and a fine-grained inner structure; composition $85TeO_2$, $15B_2O_3$, × 9000.

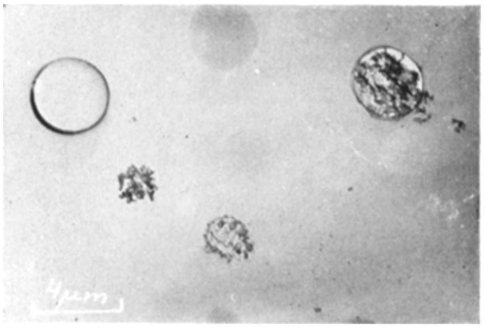

Figure 7 Replica electron micrograph illustrating "the outflow" of the fine grains in the droplet at a tearing in its envelope formed in the course of cooling, × 2250.

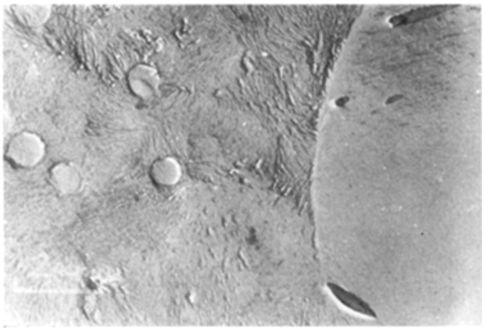

Figure 8 Replica electron micrograph of a $35TeO_2$, $65B_2O_3$ sample, containing droplets of the amorphous phase, × 7500.

sections rich in TeO_2). The basic matrix is richer in B_2O_3. The concentration distribution of tellurium in the drop (about 59.4% of Te on average) given in Fig. 10, is shown superposed on the drop image obtained by back-scattered electrons.

Structurally, the second phase is a complicated heterogeneous system. Amorphous regions of liquid microseparation are observed in it (Fig. 11). Plate-like hexagonal crystallites probably of B_2O_3 or another compound, having a diameter of ~ 5 µm are also detected in this phase (Fig. 12). The X-ray phase analysis, as well as the electron diffraction investigation of the samples, built up mainly from the second phase, reveals that these regions are amorphous. The samples,

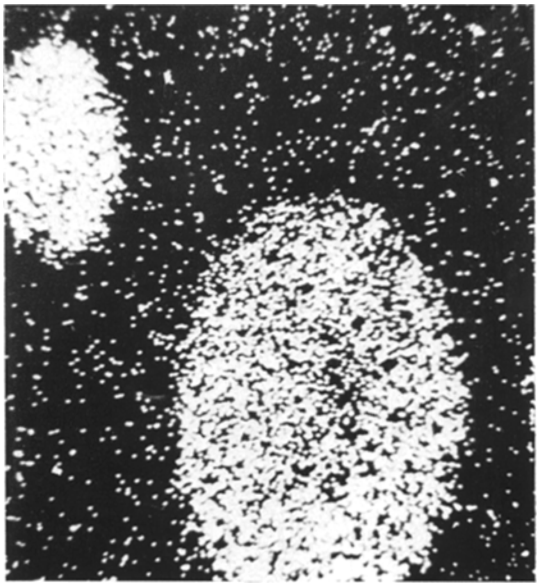

Figure 9 X-ray image of the largest drops shown in Fig. 8, × 500.

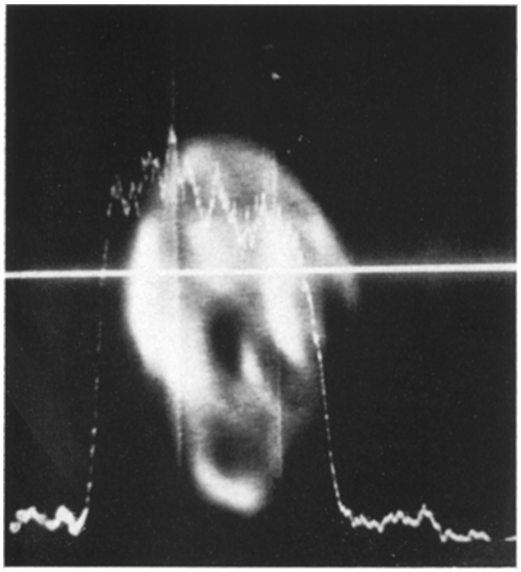

Figure 10 Back-scattered electron image and tellurium distribution in the drops shown in Fig. 9, × 500.

containing from 85 to 40 mol % TeO_2, are likewise initially amorphous, but after thermal treatment, they crystallize with the separation of only one crystalline phase, consisting entirely of TeO_2. It is also of interest to point out that the melts of certain compositions, located before point 1 in Fig. 13 (of about 80 mol % TeO_2), if cooled only to 680°C and held for 1 h, are gradually transformed into a white-milk viscous liquid, i.e. into the second phase.

4. Discussion

The experimental investigations carried out give us grounds to suggest that a wide region of well-manifested liquid–liquid phase separation exists in the TeO_2–B_2O_3 system. Taking into account the absence of other crystalline phases, with the exception of those quoted (B_2O_3 and TeO_2), on the basis of these initial investigations, the conclusion may be drawn that the phase diagram of the system studied is of a eutectic-like type, having a monotectic reaction of immiscibility (Fig. 13). In case the melt is supercooled, an immiscibility process is observed on both sides of the binodal curve, but the matrix and droplets undergo changes as the composition varies. Similar processes are observed in the CaO–SiO_2 system. Even in the case of high supercooling rates employed for compositions close to the dome of phase separation, Galahov obtained only opaque glasses [9]. Roy [10] likewise assumes that the structure of the glasses, having compositions close to the region of the stable immiscibility, is a special one. It may be assumed that the matrix before point 1 (Fig. 13) is rich in TeO_2 after immiscibility, while the droplet-like formations are composed mainly of B_2O_3. In this case, in the course of cooling, the

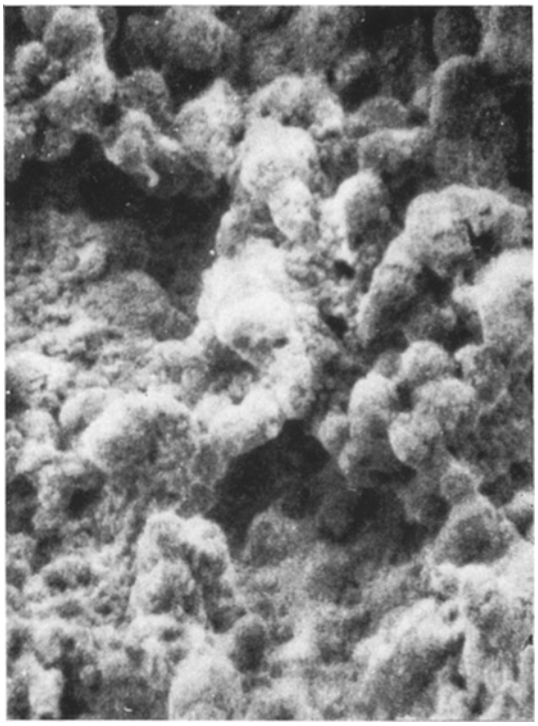

Figure 11 Secondary electron image of a $12TeO_2$, $88B_2O_3$ sample, × 1500.

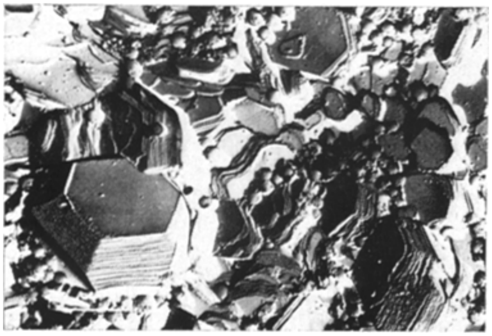

Figure 12 Replica electron micrograph of a $12TeO_2$, $88B_2O_3$ sample etched for 10 sec with a 10% hydrofluoric acid solution, × 2250.

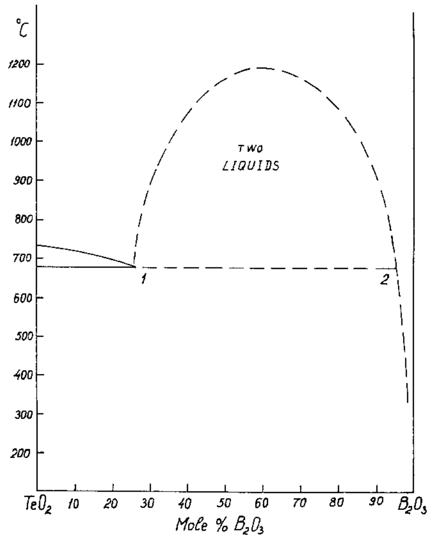

Figure 13 Phase diagram of the TeO_2–B_2O_3 system.

melt (passing below the monotectic) becomes supersaturated in B_2O_3 and a second liquid fine-scale phase, rich in B_2O_3, forms. This process gives evidence of the tendency towards realization of macro-phase separation in the melt, prevented by its cooling. According to the phase rule, two liquid (L_1 + L_2) and one crystalline phases should co-exist in equilibrium on the monotectic curve. Only after the complete transformation of L_1 into L_2 will a monovariant process take place and will, at lower temperatures, be in equilibrium with TeO_2. Because of the non-equilibrium conditions of cooling, however, we obtained one microheterogeneous structure which may change with the duration of the thermal treatment. In fact, when in a state of equilibrium (according to the phase diagram), this second phase should co-exist with the TeO_2 crystals. Therefore, in the case of the retention at ~ 680°C, a transition into the second phase is observed instead of crystallization. After point 2 (Fig. 13), the matrix is enriched in B_2O_3 and the metastable phase separation also occurs. Clear compositions are only obtained at higher rates of cooling. Irrespective of the manner in which the samples are undercooled, they are always amorphous, as already stated; thus, the question whether a glass forming region exists in the system studied is open to discussion. The question of whether we have the right to believe the opaque phase to be a glassy one is raised. It may be correct to speak about an ability of the melts of the TeO_2–B_2O_3 system to supercool into two amorphous macrophases. They take part either in a stable or in a metastable immiscibility, depending on the temperature, composition and duration of the thermal treatment. These complex aggregation phenomena lead to the formation of multiphase microheterogeneous system. Elegant examples of the simultaneous presence of 4 or 5 and more phases are described by Vogel [8]. These instances, as well as the results obtained from that investigation, should not be taken as sporadic nontypical and single phenomena. It is a well-known fact, from a thermodynamic viewpoint, that in a binary system it is not possible for more than three phases to co-exist in an equilibrium. In so far as the glass has a frozen non-equilibrium structure, the mechanism of phase changes in it could be more complicated. By analogy with the solid-state reactions, we assume that a thermodynamically stable state at the phase separation should be obtained through a series of metastable states. These immiscibility phenomena depend essentially upon the experimental conditions.

Our future investigations will endeavour to throw further light onto the kinetics of phase separation in the TeO_2–B_2O_3 system.

References

1. N. TOROPOV, V. BARZAKOVSKII, V. LAPIN and N. KURTSEVA, "Diagrammi sostoyaniya silikatnih sistem" (Nauka, Leningrad, 1969).
2. R. J. CHARLES, *J. Amer. Ceram. Soc.* **49** (1966) 55.
3. R. R. SHAW and D. R. UHLMANN, *ibid* **51** (1968) 377.
4. S. MALUTIN, Ph.D. Thesis, MHTI "D. Mendeleev" (Moskow, 1970).
5. A. YAHKIND and N. MARTYSHCHENKO, *Comm. Acad. Scis. USSR, Inorganic Materials* **6** (1970) 1459.
6. V. I. MAZEPOVA, K. K. SAMPLAVSKAYA, M. H. KARAPETYANTS and V. I. GRACHEV, *Trudi MHTI "D. Mendeleev"* **67** (1970) 45.
7. Y. DIMITRIEV, M. MARINOV, Y. IVANOVA and L. LAKOV, *Compt. Rend. Acad. Bulg. Sci.* **25** (1972) 1533.
8. W. VOGEL, W. SCHMIDT and L. HORN, *Silikattechnik* **23** (1974) 112.
9. F. GALAHOV, "Strukturnie prevrashcheniya v steklah pri povishenih temperaturah" (Nauka, Moscow, Leningrad, 1965).
10. R. ROY, *J. Amer. Ceram. Soc.* **43** (1960) 670.

Received 7 October and accepted 28 November 1974.