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THE CHARACTER OF MELTING AND PHASE CRYSTALLIZATION IN THE Bi_2O_3-B_2O_3-ZnO SYSTEM

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ABSTRACT

The processes of compound formation in a solid phase and phase separation on crystallization of glassy materials as well have been studied using the Bi_2O_3 - B_2O_3 - ZnO ternary system as an example.

INTRODUCTION

In the Bi_2O_3-B_2O_3-ZnO ternary system the processes of phase- and glass-forming have been investigated by us.Carrying out of this system triangulation required more accurate definition of the melting character of the phases,forming in the ZnO-B_2O_3 and Bi_2O_3-B_2O_3 binary systems. The thermal characteristics of glasses obtained by us have been considered according to the triangulation results of the Bi_2O_3-B_2O_3-ZnO system.

METHODS OF RESEARCH

The methods of research were the differential-thermal and X-ray diffraction methods of analysis.Thermographic investigations were carried out using " F.Paulik,J.Paulik, L.Erdey" derivatograph (Hungary) in platinum crucibles.The heating rate of the furnace was 10°/min. X-ray diffraction analysis was run using the X-ray-diffractometer DRON-3 (Cu$K\alpha$ -radiation, Ni-filter).

RESULTS AND DISCUSSION

To solve the set problem the heating thermograms of charges having the compositions corresponding to the compounds of the ZnO-B_2O_3 /1/ and Bi_2O_3-B_2O_3 /2/ binary systems were taken.

In this case it was noticed that in the thermograms of some compositions taken according to the binary systems one exoeffect was observed,in the other compositions the number of exoeffects was increased.But the rising of the exoeffect number took place

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not at random but in accordance with a number of congruent phases, preceding this phase in the binary system, if to place them in the direction of increasing of the boron oxide concentration, the temperatures of the repeated exoeffects being constant.

So, in the $ZnO-B_2O_3$ system the temperature of exoeffect equal to 610°C corresponds to the borate formation $3ZnO \cdot B_2O_3$. In charge of this composition the exoeffect at the temperature of 610°C is the only one. It is also kept in the charge of $ZnO:B_2O_3 = 1:1$ composition but in this case some more, a new exoeffect appears at the temperature of 710°C. Annealing of the charge of this composition at the temperatures of two exoeffects followed by the X-ray diffraction analysis showed that at the temperature of 610°C the formation of borate $3ZnO \cdot B_2O_3$ took place and only at the temperature of 710°C borate $ZnO \cdot B_2O_3$ was formed.

Thus, the formation of zinc borate $ZnO \cdot B_2O_3$ takes place in stages and the number of exoeffects determines the number of stages.

The similar results have been obtained for the $Bi_2O_3-B_2O_3$ system as well, where the charge of $Bi_2O_3:B_2O_3 = 1:3$ composition was characterized by the largest quantity of exoeffects. The charge of $Bi_2O_3:B_2O_3 = 1:4$ composition did not exhibit any inherent exoeffect as well as the charge of the incongruent phase of $12Bi_2O_3 \cdot B_2O_3$ composition. This has made it possible to suppose that the $Bi_2O_3 \cdot 4B_2O_3$ compound melts with decomposition but only the phases having congruent melting possess their inherent exoeffect of the formation. At the same time, the phases with the composition ratio $Bi_2O_3:B_2O_3 = 1:1$ and 5:1, not indicated in the phase diagram /2/ exhibited their inherent exoeffect of the formation. It was shown in /3,4/ the existence of the $Bi_2O_3 \cdot B_2O_3$ phase, but the authors of /5/ watched the presence of the $3Bi_2O_3 \cdot B_2O_3$ phase over the fusion of the binary system. The exoeffect temperatures of the formation for the $3Bi_2O_3 \cdot B_2O_3$ phases were 500°C, $2Bi_2O_3 \cdot B_2O_3$ - 570°C, $Bi_2O_3 \cdot B_2O_3$ - 600°C, $5Bi_2O_3 \cdot 5B_2O_3$ - 640°C, $Bi_2O_3 \cdot 3B_2O_3$ - 660°C.

The investigation of the bismuth borate structures cited in /6,7/ showed that the $2Bi_2O_3 \cdot B_2O_3$ structure must be less stable than for example, the $3Bi_2O_3 \cdot 5B_2O_3$ at the account of greater mobility of BO_3 - triangles in comparison with the $[B_5O_{11}]^{7-}$ radi-

cal. The similar situation, probably, takes place in the $ZnO-B_2O_3$ system. That is, borate formation runs in the direction from less stable low-borate compounds to more stable multi-borate structures.

On studying thermal characteristics of glasses of a ternary system it was found out that glasses corresponding to the compositions of quasi-binary sections are crystallized at the constant temperature. Thus, in the $Bi_2O_3 \cdot 3B_2O_3$ - $ZnO \cdot B_2O_3$ quasi-binary system both initial components can be in the glassy state. The crystallization temperature of $Bi_2O_3 \cdot 3B_2O_3$ was 610°C and of $ZnO \cdot B_2O_3$ was 710°C. The glasses of this system, independent on the composition, are crystallized at the temperature of 600°C, i.e. on the curve recording of glass heating we watch a common effect of crystallization. It is likely that the phases $Bi_2O_3 \cdot 3B_2O_3$ and $ZnO \cdot B_2O_3$ to be united in one structure.

The phase diagram of this system plotted on the basis of the crystallized sample study showed that the $Bi_2O_3 \cdot 3B_2O_3$-$ZnO \cdot B_2O_3$ section was of ordinary eutectic type. So, one can suppose that the basis of glass-forming must be a binary (or quasi-binary) eutectics /8/.

On investigation of glasses with non-quasi-binary sections it was established that the constant crystallization temperatures were observed in the glasses of compositions being in the limits of one secondary system.

The temperature analysis of glass crystallization in the limits of secondary systems isolated as a result of triangulation of the Bi_2O_3-B_2O_3-ZnO system showed that independent on the sections passing through one sub-system, the temperatures of glass crystallization with compositions of these sections were practically the same. For example, through the subordinate $3Bi_2O_3 \cdot 5B_2O_3$ - $Bi_2O_3 \cdot 3B_2O_3$ - $3ZnO \cdot B_2O_3$ system a part of compositions pass along two sections: $3Bi_2O_3 \cdot 5B_2O_3$ - $ZnO \cdot B_2O_3$ and $2Bi_2O_3 \cdot B_2O_3$ - $ZnO \cdot B_2O_3$. In the indicated composition ranges in glasses of $3Bi_2O_3 \cdot 5B_2O_3$ - $ZnO \cdot B_2O_3$ section the temperature of crystallization is 590°C, in glasses of $2Bi_2O_3 \cdot B_2O_3$ - $ZnO \cdot B_2O_3$ section the temperature of crystallization is also 590-600°C.

Thus, in the secondary ternary system a single basis of glass structure formation must also exist, that is, probably, a ternary eutectics.

CONCLUSION

On the research of interaction processes of boron oxide with bismuth oxide or zink oxide it was shown that the inherent exoeffect of formation with definite initial temperature corresponded to every congruently melting compound.

It is also established the correlation of thermal characteristics of glasses with location of ternary eutectics and their phase ranges in the glass-forming part of the Bi_2O_3-B_2O_3-ZnO ternary system.

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