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PHASE EQUILIBRIUM IN THE SeO_2–Bi_2O_3 SYSTEM*

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Abstract

The subject of the present study is the system SeO_2–Bi_2O_3 that comprises two oxides with low melting points. All batches are thermal treatment in quartz ampoules, which are evacuated and sealed at a pressure P=0.1 Pa. On the basis of DTA (differential thermal analysis) and X-ray data, the most probable liquidus line of the system has been plotted. The eutectic composition lies about 90 mol% SeO_2, with on eutectic temperature at 230°C. Above 20 mol% Bi_2O_3 the liquidus temperature extremely increases. The formation of three compounds is proved: $Bi_2Se_3O_9$ and $Bi_2Se_4O_{11}$ are melting incongruently at 540 and 350°C respectively and Bi_2SeO_5 congruently at 915°C.

Keywords: congruent melting, eutectic, incongruent melting, liquidus, peritectic, phase equilibrium

Introduction

The investigations of bismuth selenites started with the preparation of two phases $Bi_2Se_3O_9$ and $Bi_2Se_3O_9{\cdot}H_2SeO_3$ by precipitation from solutions [1–3]. It was found that the phase $Bi_2Se_3O_9$ is thermally stable up to 550°C. Dolgikh [4] confirmed the existence of this phase. Above 580°C he found 3 new phases: $Bi_{18}SeO_{29}$, Bi_4SeO_8, Bi_6SeO_{11}. They can be considered as a result of structure distortion of the initial compound δBi_2O_3 and represent a homologous series of fluorite like structure of the type $Bi_{1-x}Se_xO_{3+1/2\ \ 1-x/2}$. The phase formation in the ternary system Bi–Se–O has been investigated by Operman *et al.* [5]. On the basis of X-ray studies they assumed the formation of a phase with the composition $Bi_2Se_4O_{11}$. In addition, there is also X-ray data for the phase Bi_2SeO_2 [6].

The purpose of this study is to investigate compositions in the low temperature range of the SeO_2–Bi_2O_3 system because they are of essential interest in order to elucidate the synthesis conditions of the multicomponent selenite glasses and glass-ceramic materials.

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Experimental

Solid state synthesis is applied in our studies instead of the preparation from solutions [1–3]. The experiments have been carried out using SeO_2 and Bi_2O_3 (p.a.). The batches were prepared through 5 mol% in the concentration range of 50–100 mol% SeO_2 and around supposed eutectic point through 2.5 mol%. By the way, the compositions with the ratio of the initial oxides corresponding to the crystalline phases described in the literature were also selected. In order to avoid hydration, the batches were prepared in a drying box. After that they were transferred to quartz ampoules, evacuated and molten at P=0.1 Pa. The ampoules have a volume V=2 cm^3 and contain about 1 g of the batch. The samples prepared in this way were subjected to thermal analysis (heating rate 10° min^{-1}) and isothermal treatment at constant temperatures before and after the main exothermic and endothermic effects.

Results and discussion

DTA data on some compositions are presented in Fig. 1 where the complex character of the transformations with rising temperature is illustrated. The first endothermic effect appears at about 100°C and is due to the elimination of the residual water. In order to elucidate the phase formation mechanism, isothermal synthesis of various compositions at temperatures corresponding to the endothermic and exothermic effects was performed. The phase corresponding to 1:1 ratio of SeO_2:Bi_2O_3 was synthesized by a solid phase reaction at the temperature of the exothermic effect at 400°C for 10 h.

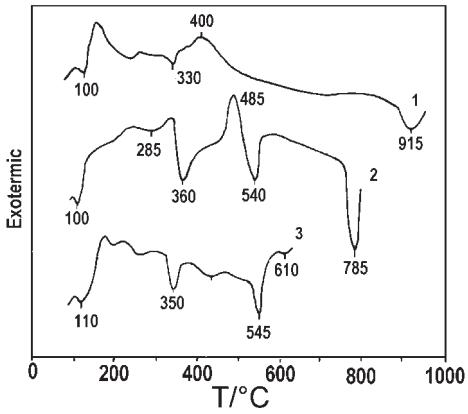

Fig. 1 DTA curves of 1 – Bi_2SeO_5; 2 – $Bi_2Se_3O_9$; 3 – $Bi_2Se_4O_{11}$

The next two endothermic effects are in the range 350–550°C. A composition with Bi_2O_3:SeO_2=1:3, which corresponds to the phase $Bi_2Se_3O_9$, was heated at 300°C for 20 h. According to the X-ray analysis, the product obtained represents a mixture of two phases: $Bi_2Se_3O_9$ (1:3) and $Bi_2Se_4O_{11}$ (1:4).

After thermal treatment at 450°C for 20 h, a mixture of $Bi_2Se_3O_9$ and SeO_2 was obtained. At this temperature $Bi_2Se_4O_{11}$ decomposes and the amount of $Bi_2Se_3O_9$ continuously increases. The same composition treated at 540°C for 20 h yields the Bi_2SeO_5 phase, i.e. above this temperature the compound $Bi_2Se_3O_9$ (1:3) decomposes.

A composition with SeO_2:Bi_2O_3=4:1 was heated at 300°C for 10 h. As a result of the solid phase reaction, $Bi_2Se_4O_{11}$ was obtained. The same sample heated at 400°C yielded SeO_2 and $Bi_2Se_3O_9$. Hence, the endothermic effect at 540°C should be considered due to $Bi_2Se_3O_9$ dissociation. All compositions, which are between 80 and 100 mol% SeO_2, are characterized by one endothermic effect, which is within the range of 200–300°C. This indicates that near SeO_2 site a low-melting eutectic is formed. On the basis of all DTA and X-ray data the most probable liquids line of the system has been plotted (Fig. 2). It is possible to make a comparison with our previous results for the selenite phase diagrams [7–9]. In the system SeO_2–TeO_2 an eutectic about 75 mol% SeO_2 was found and T_E=320±5°C. The formation of a new phase with a composition SeO_2:TeO_2=1:1 was proved [7]. The existence of only one incongruently melting compound $2SeO_2 \cdot V_2O_5$ was established in the system SeO_2–V_2O_5 [8]. The eutectic point lies at about 96.5 mol% SeO_2 and T_E=250±5°C. The phase diagram of the system SeO_2–MoO_3 is of a simple eutectic type [9]. The eutectic composition lies at about 90 mol% SeO_2, and T_E=250±5°C. All these systems are suitable for the synthesis of multicomponent selenite glasses, especially in the concentration range around the eutectic points. In this relation the obtained data for the SeO_2–Bi_2O_3 phase diagram outline good perspective for the production of new glasses. Indeed, all glass compositions in the systems SeO_2–Bi_2O_3–M_nO_m are situated near the eutectic point of the binary system [10, 11]. They are with a better chemical resistance than glasses in other systems.

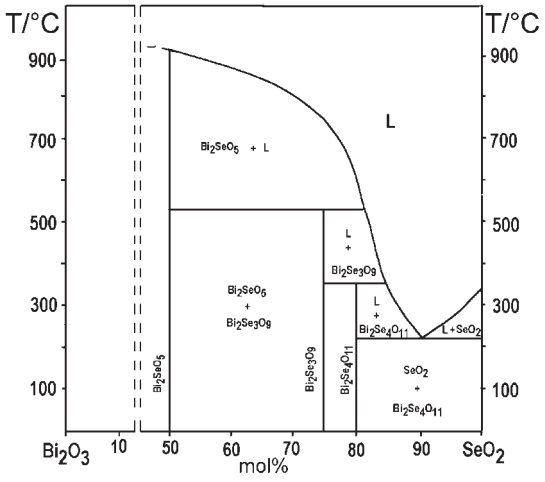

Fig. 2 Phase diagram of the SeO_2–Bi_2O_3 system

Conclusions

A part of the phase diagram of system Bi_2O_3–SeO_2 built up in the low temperature range near SeO_2 side. The introduction of more than 20 mol% Bi_2O_3 leads to a sharp increase of the liquidus temperature. It has been confirmed that between 50–100 mol% SeO_2 three compounds are formed: Bi_2SeO_5, $Bi_2Se_4O_{11}$ and $Bi_2Se_3O_9$. It has been proved that the compounds: $Bi_2Se_3O_9$ and $Bi_2Se_4O_{11}$ melt incongruently, while Bi_2SeO_5 melts congruently. The present phase diagram of the Bi_2O_3–SeO_2 system is in agreement with the results for other available equilibrium systems: SeO_2–MoO_3, SeO_2–V_2O_5 and SeO_2–TeO_2. Their eutectic temperatures are below 320°C and corresponding compositions are very suitable for synthesis of many-component selenite glasses, in which the main network former is SeO_2

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