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The 0.21 atm P_{O_2} isobar in the CuO–$CuO_{0.5}$–$BiO_{1.5}$ system

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Abstract

Equilibrium relationships in the $BiO_{1.5}$–Cu_2O–CuO system were investigated as a function of temperature under atmospheric pressure. From the results obtained, the position of the 0.21 atm P_{O_2} isobar was established and is shown on a ternary phase diagram.

INTRODUCTION

The Bi–Sr–Ca–Cu–O system, in which superconducting crystals with $T_c = 81°C$ have been obtained [1], is of considerable interest.

The high temperature phase equilibria of this system have not been practically studied. Its subsystems, including Bi–Cu–O, also require consideration. Two papers [2,3] have been published on the Bi–Cu–O system: they report different versions of the $BiO_{1.5}$–CuO binary diagram.

The eutectic formed by an intermediate compound with bismuth oxide is present in both versions, its coordinates being 91.16 mol.% $BiO_{1.5}$ (770°C) [2] and 94.8 mol.% $BiO_{1.5}$ (600°C) [3]. Thus, the intermediate compound has the composition $2BiO_{1.5} \cdot CuO$ according to ref. 2 and $4BiO_{1.5} \cdot CuO$ according to ref. 3. In addition, in ref. 2, a second eutectic with coordinates 57 mol.% $BiO_{1.5}$ and 845°C is established. These discrepancies should be elucidated.

EXPERIMENTAL

Because the experimental technique used here involved heating mixtures in air, our diagram represents the CuO–Cu_2O–$Bi_{1.5}O$ ternary system, because the oxidation state of the copper is a function of the temperature and the oxygen pressure in the gas phase. The stages of the sample dissociation in such a system indicate the type of phase equilibria present and were followed by means of a thermobalance [4].

Thus, thermogravimetry is the main method of analysis, performed using a Derivatograph-C (Hungary). The initial materials are CuO (99.99% purity;

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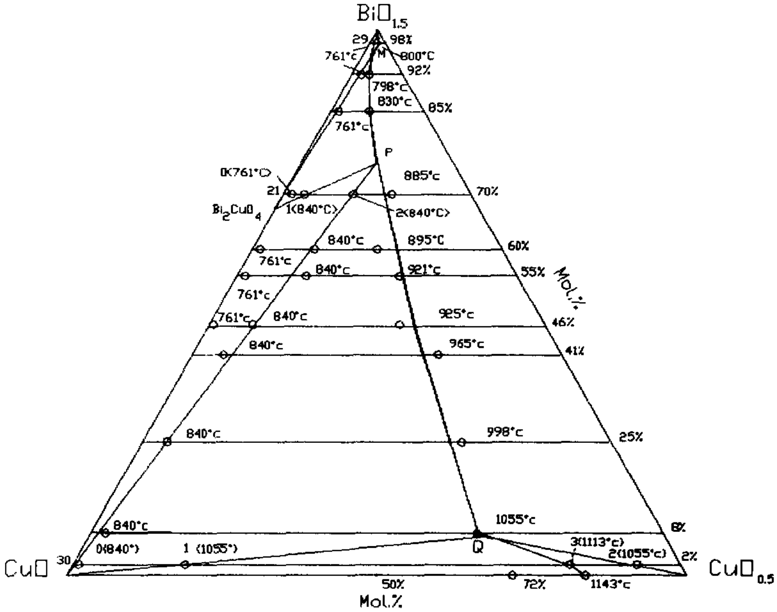

Fig. 1. Phase triangle of the system $BiO_{0.5}$–CuO–$CuO_{0.5}$ with projection of the isobar curve at an oxygen partial pressure of 0.21 atm.

melting temperature, 1143 °C) in our experiments, and about one percent content of Cu_2O and Bi_2O_3 (99.99% purity; melting temperature, 806 °C). The conditions for the DTA analyses were identical for all the samples: the mass of the mixed oxides CuO and $BiO_{1.5}$ was always 100 mg; the heating rate was 7 °C min^{-1} in Al_2O_3 crucibles in air under atmospheric pressure. The accuracy of the measurements was 0.2 mg for mass and 10 °C for temperature (characteristics of the apparatus).

RESULTS AND DISCUSSION

The results obtained are shown in Fig. 1, which displays a phase triangle as the basis of a three-dimensional equilibrium diagram of the $BiO_{1.5}$–CuO–$CuO_{0.5}$ system with a projection of the liquidus surface isobar onto it. The composition and phase changes which can occur on heating at constant pressure are indicated on this figure.

The choice of the phase triangle coordinates is conditioned by the fact that in this case the $BiO_{1.5}$ molar fraction remains constant while the sample composition changes; thus the point representing the total composition of the sample will move along a line parallel to the CuO–$CuO_{0.5}$ side as the experiment proceeds.

In the case of a 2% $BiO_{1.5}$ content, the phase transitions are presumed to occur as follows. At room temperature the initial position of the mixture is marked by point 30. With increasing temperature, the mixture partly melts and loses oxygen, when peritectic reaction takes place at 840 °C. The total composition of the mixture passes from point 30 to 0 (840 °C). As the temperature increases from 840 to 1055 °C, the figurative point of the liquid composition moves along the isobar from P to Q, whereas the total composition of the mixture goes from 0 (840 °C) to 1 (1055 °C). Liquid Q, belonging to the binary eutectic curve 72%–S is in equilibrium with CuO and $CuO_{0.5}$. The dissociation process occurs at a constant temperature with the subsequent formation of $CuO_{0.5}$, the total composition of the sample changing from 1 (1055 °C) to 2 (1055 °C).

When the temperature exceeds 1055 °C the composition of the liquid begins to shift from Q to 3 (1113 °C). As this proceeds, oxygen enters the system and the figurative point of the mixture composition passes from 2 (1055 °C) to 3 (1113 °C). The point 3 (1113 °C) corresponds to complete melting of the sample at the given P_{O_2} (0.21 atm), so that here the figurative point of the liquid coincides with that of the total composition.

Another example is a sample with $BiO_{1.5} = 70$ mol.%. At 761 °C in a tested sample, the eutetic liquid 'M' is generated. With further heating the liquid composition varies according to the MP isobar, and the total composition of the mixture changes from 0 (761 °C) to 1 (840 °C). At point 1 (840 °C) the sample starts losing oxygen rapidly, as Bi_2CuO_4 dissociates at a constant temperature (non-variant point P). Complete melting occurs at 885 °C.

In a mixture with 98 mol.% $BiO_{1.5}$ at 761 °C a binary eutectic liquid M is formed. With further increase in temperature the sample continues losing

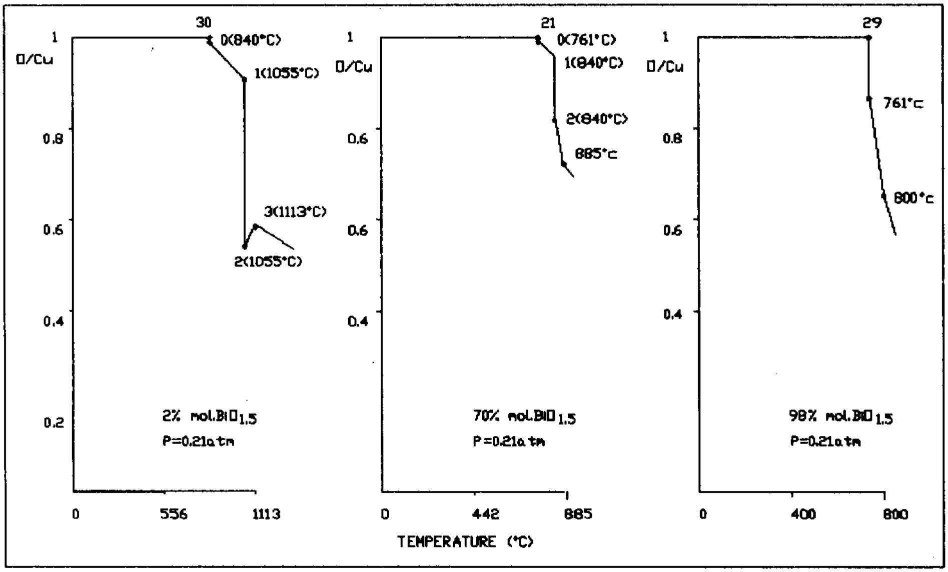

Fig. 2. Dissociation curves of $CuO–BiO_{1.5}$ heated in air. Atomic ratio, O/Cu, plotted against temperature.

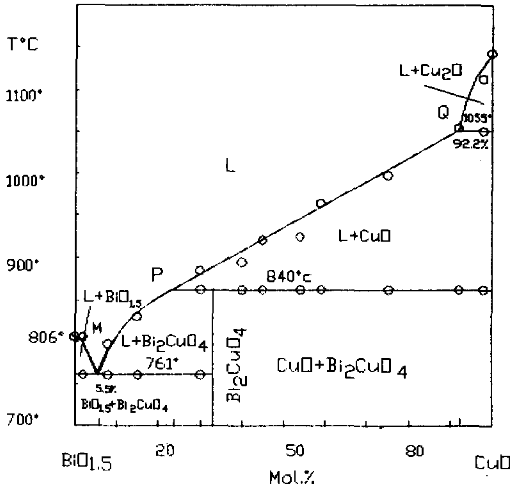

Fig. 3. Isobar projection on the CuO–$BiO_{1.5}$ side of the CuO–$CuO_{0.5}$–$BiO_{1.5}$ triangle.

oxygen and melts completely at 800 °C. Figure 2 shows the dissociation curves of the samples with different $BiO_{1.5}$ contents, the ratio of O/Cu atomic fractions being plotted against temperature.

The location of the CuO–$CuO_{0.5}$ eutectic point is taken from ref. 5. The point of intersection of the isobar and the CuO–$CuO_{0.5}$ side has been found experimentally.

It should be noted that the DTA effects fixed at 761 °C for the samples with 46, 55 and 60 mol.% $BiO_{1.5}$ are non-equilibrium ones because the initial mixtures were CuO and $BiO_{1.5}$ oxides, and not an intermediate compound and copper oxide.

Figure 3 depicts the isobar curve projected onto the CuO–$BiO_{1.5}$ side of the triangle along the lines of variation of the sample total composition. The $BiO_{1.5}$–Bi_2CuO_4 eutectic in this case has the coordinates 94.5 mol.% $BiO_{1.5}$ and 761 °C.

The compound Bi_2CuO_4, mentioned in ref. 2, was confirmed by X-ray studies of the samples. Its dissociation takes place at 840 °C.

Thus three non-variant points were observed in the $BiO_{1.5}$–CuO–$CuO_{0.5}$ system at atmospheric pressure:

Cotectics: $BiO_{1.5}$ + Bi_2CuO_4–L + O_2, 5.5 mol.% CuO, 761 °C.

Peritectics: Bi_2CuO_4–CuO + L + O_2, 23 mol.% CuO, 840 °C.

Cotectics: CuO + Cu_2O–L + O_2, 92.2 mol.% CuO, 1055 °C.

CONCLUSIONS

The $BiO_{1.5}$–CuO system has been considered as a ternary $BiO_{1.5}$–CuO–$CuO_{0.5}$ system.

An isobar ($P_{O_2} = 0.21$ atm) curve has been constructed, i.e. the temperature and composition of the liquid curve at atmospheric pressure have been established.

Under these conditions, the system has been found to have one intermediate compound, Bi_2CuO_4, melting incongruently at 840 ° C.

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