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Phase Equilibria in the Ca–Cu–O System Under Variable Temperatures and Oxygen Pressures

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Abstract: Synthesis of samples in the Ca–Cu–O system in air by the ceramic method was carried out. Existence of Ca_2CuO_3 and $CaCu_2O_3$ compounds was confirmed. Phase equilibria during thermal dissociation of Ca_2CuO_3 and its mixtures with CaO and CuO (953–1173K) were studied by the circulation method, in addition to the EMF method and X-ray phase analysis.

The results are shown as in isothermal section (1073K) of the Ca–Cu–O phase diagram (P_{O2}–x diagram) and its projection on the P_{O2}–T plane. Thermodynamic analysis was also performed.

1 INTRODUCTION

Early mention of studying the Ca–Cu–O system dates to 1936.[1] In that paper a fragment of the state diagram of the CaO–Cu_2O system is presented and the eutectic location is determined. The existence of compounds or solid solutions was not noted. Unfortunately, the authors did not indicate the oxygen pressure of interest. It is known, however, that the oxygen pressure has an essential effect on the view of phase diagram. An illustration is in Ref. 2 where state diagrams of the CaO–CuO ($\frac{1}{2}Cu_2O$) system constructed in air and in an oxygen atmosphere are given. The comparison shows that decreasing oxygen pressure leads not only to quantitative changes (decrease in eutectic temperature and decomposition of the Ca_2CuO_3 compound, change in eutectic composition) but to qualitative changes (appearance of a new phase region due to formation of the Cu_2O compound in air) as well. The existence of Ca_2CuO_3 noted in that work is confirmed by the data.[3-7] This compound has the orthorhombic crystal lattice (Immm), the unit cell parameters are $a = 1{\cdot}223(9)$ nm, $b = 0{\cdot}377(9)$ nm, $c = 0{\cdot}325(9)$[3] and $a = 1{\cdot}2243$ nm, $b = 0{\cdot}3779$ nm, $c = 0{\cdot}3258$ nm.[6]

Apart from Ca_2CuO_3, information on the $CaCu_2O_3$ compound is available in the literature.[5,7,8] It has the orthorhombic crystal lattice (Pmmm) with the following unit cell parameters: $a = 0{\cdot}985$ nm, $d = 0{\cdot}411$ nm, $c = 0{\cdot}347$ nm.[8] The fact that $CaCu_2O_3$ was not observed by some investigators is probably explained by the fact that this compound exists in the narrow temperature interval (~ 40°) close to the eutectic melting temperature.[7]

In several papers[7,9,10] one more composition is mentioned, namely, $CaCuO_2$ ($Ca_{1-x}CuO_2$). Crystallochemical data on this compound are given in Refs 7 and 10 and superstructures have been observed in both works, but there are disagreements on interpretation. Other attempts[3,5,11] to obtain this compound were unsuccessful.

The most complete state diagram of the Ca–Cu–O system in air is presented in Ref. 7. However, we have no literature data on phase equilibria under lower oxygen pressures.

2 EXPERIMENTAL

Initial samples of different compositions were obtained by the ceramic technique from CuO and $CaCO_3$ of CDA-type (pure for analysis). Powdered components in various proportions were mixed in Fritsch planetary mill under ethyl alcohol for 30 min. The mixture was pressed under a pressure of 1 MPa into pellets with diameter of 14 mm and thickness of 4 mm. Firing was performed at

700–1000°C in a SNOL-type muffle furnace in air. The duration of firing was 5–200 h according to the temperature of interest. From time to time, the samples were quenched in air and tested by X-ray phase analysis (diffractometer DRON-3.0, monochromatized CuK$_\alpha$ radiation). The completion of the solid-phase reaction was judged by the appearance of an invariable phase pattern and a constant unit cell parameter of the phases formed.

For investigating heterogeneous equilibria the static method was applied making use of the vacuum circulatory installation, in which the oxygen pressure measurements were carried out continuously by the EMF method with a solid electrolyte.[12] The essence of that technique implies that an exactly measured small amount of oxygen is removed from the initial sample, and solid and gas phases are brought to an equilibrium state. The attainment of the equilibrium state was determined from the fact that partial oxygen pressure above the sample remained unchanged for several hours. To avoid obtaining metastable states an equilibrium was attained both from the dissociation side and from the oxidation one. Every now and then, to get one-to-one relation between oxygen pressure and phase constitution of dissociation products, the sample of interest was quenched (without decompression of the installation) and tested by X-ray phase analysis.

Up to 1173 K the circulatory installation used guaranteed the maintenance of temperature with an accuracy of ±3°C. The determination of partial oxygen pressure $\log P_{O2} = \pm 0{,}1$ and the amount of oxygen removed from the sample was ± 1 atom%.

The same installation was used for synthesizing samples at lower oxygen pressures.

3 RESULTS AND DISCUSSION

The Ca_2CuO_3 single-phase sample was obtained after a 5-h annealing at 1223K. It had the orthorhombic crystal lattice with the following unit cell parameters: $a = 1{\cdot}2244(1)$ nm, $b = 0{\cdot}3777(1)$ nm, $c = 0{\cdot}3259(1)$ nm. The production of completely single-phase $CaCu_2O_3$ compound was unsuccessful. Even after annealing for 200 h at 1273 K, traces of Ca_2CuO_3 and CuO were found. In our opinion it is due to some temperature gradient within the furnace during annealing. The unit cell parameters of $CaCu_2O_3$ obtained were as follows: $a = 0{\cdot}9965(6)$nm, $b = 0{\cdot}4087(2)$nm, $c = 0{\cdot}3469(1)$ nm.

Synthesis of $CaCuO_2$ was attempted at 973 and 1073 K. But even after 200-h annealing, no traces of this compound were observed. On the X-ray patterns only reflections of Ca_2CuO_3 and CuO were found.

Construction of the 'P–T–x' state diagram of the Ca–Cu–O system was begun by studying dissociation processes of the samples with different composition at 1073 K. Let us take Ca_2CuO_3 as an example. It was found that this compound is stable up to the oxygen pressure of $\log P_{O2} = 1{,}8$ (Pa) (1073K). At that pressure its dissociation starts according to the reaction:

$$Ca_2CuO_3 = 2CaO + \tfrac{1}{2}Cu_2O + \tfrac{1}{4}O_2 \qquad (1)$$

As the oxygen is removed, the amount of Ca_2CuO_3 is decreased and that of CaO and Cu_2O is increased. The oxygen pressure remains unchanged.

At the low-oxygen boundary of the homogeneous region the unit cell parameters are slightly different from the initial ones: $a = 1{\cdot}2235(2)$ nm, $b = 0{\cdot}3778(1)$ nm, $c = 0{\cdot}3257(1)$ nm. It attests indirectly to the lack of significant changes of the oxygen non-stoichiometry. When ~17% of the oxygen is removed from the sample Ca_2CuO_3 disappears completely. While decreasing the oxygen pressure from $\log P_{O2} = 1{,}8$ (Pa) to $\log P_{O2} = -\ 3{,}8$ (Pa) the phase pattern (CaO + Cu_2O) is not changed: at $\log P_{O2} = -\ 3{,}8$ (Pa) the Cu_2O dissociation process starts according to the reaction:[2]

$$Cu_2O = 2Cu + \tfrac{1}{2}O_2 \qquad (2)$$

When another ~17% of oxygen is removed from the sample the process is over. So under the experimental conditions the resulting products of dissociation are CaO and Cu. While studying the dissociation of samples with the other composition one more phase equilibrium was found at $\log P_{O2} = 2$ (Pa):

$$CuO = \tfrac{1}{2}Cu_2O + \tfrac{1}{4}O_2 \qquad (3)$$

The fact that the oxygen pressure for equilibria (2) and (3) in the presence of CaO is coincident with pressure for these equilibria in the uncombined state attests to very slight solubility of CaO in CuO and Cu_2O. Although the $CaCu_2O_3$ compound does not exist in air at this temperature one can suppose that a decrease of oxygen pressure is able to somewhat change the temperature stability range. As a check on this hypothesis the composition of Ca/Cu = 1/2 was studied extensively. The $CaCO_3$ and CuO mixtures were annealed in the oxygen-controlled atmosphere at 1073 K. The oxygen pressure for each annealing is shown within the circle in Fig. 1. The annealing duration was 48 h. No traces of $CaCu_2O_3$ were observed in any experiment; an attempt to synthesize this compound at 1173 K was also unsuccessful. Because of the apparatus' limited potentialities further temperature increase was not performed.

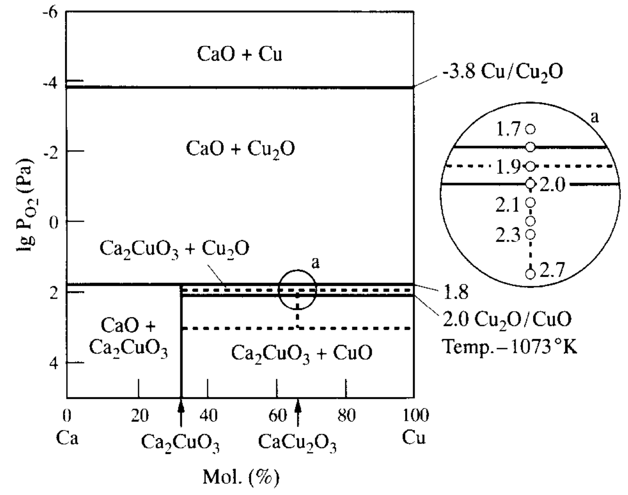

Fig. 1. Isothermal section of the '*P–T–x*' phase diagram of the Ca–Cu–O system at 1073K.

Isothermal section of the '*P–T–x*' diagram of the Ca–Cu–O system at 1073 K is presented in Fig. 1. Five phase regions observed are indicated in the figure. Moreover, it is not improbable that with increasing temperature another three phase regions will occur at the expense of formation of $CaCu_2O_3$: namely, Ca_2CuO_3 + $CaCu_2O_3$, $CaCu_2O_3$ + Cu_2O and $CaCu_2O_3$ + CuO. Their possible boundary location is qualitatively denoted by the dashed line in Fig. 1.

In order to construct the analogous isothermal sections at other temperatures, temperature dependence of equilibrium partial oxygen pressure for the Ca_2CuO_3–CaO–Cu_2O–O_2 equilibrium (reaction (1)) in the 953–1173 K range was measured:

$$\log P_{O2} = 15{\cdot}04 - 1{\cdot}44\,\frac{10^4}{T} \pm 0{\cdot}01\ (\mathrm{Pa}) \qquad (4)$$

The data on the oxygen pressure above the Cu/Cu_2O and Cu_2O/CuO mixtures are available in literature.[13]

Using these data, thermodynamic functions of Ca_2CuO_3 formation from oxides according to the reaction:

$$2CaO + CuO = Ca_2CuO_3, \qquad (5)$$

derived from combining reactions (1) and (3), can be calculated. Using known relations between Gibbs energy and temperature dependences of oxygen pressure for reactions (1) and (3) we obtain:

$$\Delta\, G_5^{\circ} = -\,3130 + 0.6T \pm 440 \qquad (6)$$

The Gibbs energy for reaction (5) of Ca_2CuO_3 formation from the oxides is seen to be slightly dependent on temperature. The closeness of equilibrium partial oxygen pressure values for the reactions of Ca_2CuO_3 and CuO dissociation within the entire temperature range of interest is considered to be an additional argument.

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