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Thermodynamic properties of binary copper (I) oxides

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Abstract

Phase equilibria during thermal dissociation and oxidation of the compounds $BaCu_2O_2$, $SrCu_2O_2$ and $YCuO_2$ were studied by the static method combined with e.m.f. method and X-ray phase analysis. The thermodynamic functions (enthalpy, entropy, Gibbs free energy change) of both these reactions and formation of the compounds from oxides were calculated.

Keywords: C. Superconductivity; Oxides; Copper (I); Phase equilibria; Oxygen pressure; Thermodynamic properties

1. Introduction

Scientific interest in the thermodynamic properties of $BaCu_2O_2$, $SrCu_2O_2$, and $YCuO_2$ is due to the role of these compounds in the synthesis of multicomponent oxide superconductive materials. Analysis of the literature data [1–11]shows that the reported thermodynamic properties of these compounds do not correlate, even when the same methodology is used.

2. Experimental

The compounds $SrCu_2O_2$, $BaCu_2O_2$, $YCuO_2$ were prepared by conventional ceramic technique from powders CuO, Y_2O_3, BaO_2, $CaCO_3$, $SrCO_3$ of pure analytical grade.

Powdered components in necessary proportion were mixed in a Fritsch planetary mill in ethanol for 30 min. The mixtures were pressed into pellets 10 mm in diameter and 2–3 mm thick under a pressure of 10 MPa.

Annealing was carried out in a gas-tight reaction tube; the partial oxygen pressure was controlled by an oxygen sensor based on $ZrO_2(Y_2O_3)$ solid electrolyte. The temperature of annealing depended on the sample: 800, 850, and 920°C for $BaCu_2O_2$, $SrCu_2O_2$ and $YCuO_2$, respectively. After each 24 h of annealing the sample was quenched hermetically in the water-cooled zone of the reaction tube and tested by X-ray phase analysis (diffractometer DRON-3.0, monochromatized CuK_α, radiation).

For investigating dissociation of the synthesized compounds the static method was applied using a vacuum circulation assembly [11]. The oxygen pressure was determined continuously by the e.m.f. method with a solid electrolyte as previously described [12]. The main advantage, compared to the e.m.f. method, is the possibility of using X-ray analysis to identify quenched solid phases, which guarantees unambiguous relation between oxygen pressure and composition of solid coexisting in equilibrium.

3. Results and discussion

The single-phase samples $BaCu_2O_2$, $SrCu_2O_2$ and $YCuO_2$ were obtained after 200, 48, 60-h annealing, respectively. $BaCu_2O_2$, is tetragonal, $D_{4h} = Y4_1$ /amd, with the following cell parameters $a = 0{,}5715$ (3) nm, $c =$ (1.0062 (8) nm, in agreement with Ref. [13]. At 800°C the low-oxygen boundary of the homogeneous region has unit cell parameters: $a = 057206$ (4) nm, $c = 1.0066$ (1) nm, which differ slightly from the initial ones. This change seems to be a consequence of decrease of oxygen content in $BaCu_2O_2$ in response to decreasing its pressure in a gas phase. But the change of the composition of $BaCu_2O_2$ on oxygen is less than 1.0 atom%, so it is not well fixed by the experimental methods used.

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At 850°C, $SrCu_2O_2$ is stable at $1gPo_2(Pa) = 2.5 \sim 5.2$. The unit cell parameters of the samples synthesized under different oxygen pressures remain practically unchanged $a = 0.5469$ (1) nm, $c = 0.9826$ (2) nm (tetragonal syngony) and correlate with Ref. [14]. It confirms the conclusion, [3–6] that oxygen non-stoichiometry of $SrCu_2O_2$ changes only slightly.

The unit cell parameters of rhombohedral $YCuO_2$, R3m [15], are $a = 0.3521$ (1) nm, $c = 1.7115$ (2) nm and are lower than reported [15]. While removing oxygen, the parameters are unchanged.

The thermal dissociation reactions of the obtained compounds were determined:

$$BaCu_2O_2 = BaO + 2Cu + 1/2O_2 \quad (1)$$

$$SrCu_2O_2 = SrO + 2Cu + 1/2O_2 \quad (2)$$

$$YCuO_2 = 1/2Y_2O_3 + Cu + 1/4O_2 \quad (3)$$

Temperature dependencies of equilibrium partial oxygen pressure (Pa) for the revealed equilibria in the 973–1173 K range were measured:

$$\begin{aligned} &\mathrm{Ig}Po_2 = 13.75 - 2.12 \times 10^4/T \pm 0.002 \\ &T = 973 \sim 1173\mathrm{K} \end{aligned} \quad (4)$$

$$\begin{aligned} &\mathrm{Ig}Po_2 = 13.1 - 2.04 \times 10^4/T \pm 0.06 \\ &T = 973 \sim 1273\mathrm{K} \end{aligned} \quad (5)$$

$$\begin{aligned} &\mathrm{Ig}Po_2 = 14.37 - 2.0 \times 10^4/T \pm 0.13 \\ &T = 973 \sim 1173\mathrm{K} \end{aligned} \quad (6)$$

Based on these data, temperature dependencies of the Gibbs free energy changes for reactions [1–3] were calculated:

$$\Delta G^\circ(1) = 203260 - 83.97T \pm 227 \text{ J mol}^{-1} \quad (7)$$

$$\Delta G^\circ(2) = 196120 - 78.31T \pm 5380 \text{ J mol}^{-1} \quad (8)$$

$$\Delta G^\circ(3) = 96900 - 45.0T \pm 3000 \text{ J mol}^{-1} \quad (9)$$

The thermodynamic data for the reaction:

$$2Cu + 1/2O_2 = Cu_2O \quad (10)$$

$$\Delta G^\circ(10) = -167053 + 71.176T \pm 272 \text{ J mol}^{-1} \quad (11)$$

were taken from Ref. [16].

Using these data, the Gibbs free energy changes of formation of all above-mentioned compounds from oxides according to the reactions:

$$BaO + Cu_2O = BaCu_2O_2 \quad (12)$$

$$SrO + Cu_2O = SrCu_2O_2 \quad (13)$$

$$1/2Y_2O_3 + 1/2Cu_2O = YCuO_2 \quad (14)$$

were derived as

$$\Delta G^\circ(12) = -36205 + 12.8T \pm 500 \text{ J mol}^{-1} \quad (15)$$

$$\Delta G^\circ(13) = -29100 + 7.13T \pm 5700 \text{ J mol}^{-1} \quad (16)$$

$$\Delta G^\circ(14) = -13400 + 9.45T \pm 3140 \text{ J mol}^{-1} \quad (17)$$

Hence reliable data may be obtained in result of joint data proccessing of independent investigations carried out by different methods. Contrary to previous works, in present research thermodynamic properties of the compounds are determined studying their thermal dissociation by the static method [11,12].

4. Conclusions

We studied phase equilibria during thermal dissociation of $BaCu_20_2$, $YCuO_2$, $SrCu_2O_2$, by the circulation method combined with e.m.f. method and X-ray phase analysis. All these compounds were found to dissociate at lower partial oxygen pressures than Cu_2O. The decomposition partial oxygen pressures of $SrCu_2O_2$ and $BaCu_2O_2$ are similar, probably as a consequence of the isomorphism of their structures. $BaCu_20_2$ is more thermodynamically stable at the high-oxygen boundary than is $SrCu_2O_2$ and $YCuO_2$. The thermodynamic functions (enthalpy, entropy, Gibbs free energy change) of both dissociation and formation of these compounds from oxides were calculated.

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