THERMODYNAMIC STABILITY OF PHASES IN THE Bi–Sr–Cu–(O) SYSTEM

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Abstract

An effort for a better understanding of the phase formation and their stability in the ternary system Bi₂O₃–SrO–CuO led to investigations of the phase equilibria, particularly in the sub-solidus region. To extend this phase region about the respective solid-liquid equilibria the isothermal and pseudobinary cuts of the BiO₁.₅–SrO–CuO ternary system in the temperature range from 810 to 850°C were determined. A particular attention was also devoted to the thermodynamic stability of the Bi₂₊ₓSr₂₋ₚCuOₓ₆₋ₘ phase.

Keywords: bismuth phase superconductors, DTA, phase diagram, solid-liquid equilibria, superconducting phase, X-ray analysis

Introduction

In spite of a relatively long time since the first report on the superconductivity in ternary bismuth cuprates an interest about them still outlasts. The superconducting bismuth cuprates form a family of phases with a layered structure. Their composition can be formally expressed by the general formula Bi₂Sr₂Caₙ₋₁CuₙO₄₊₂ₙ with n = 1, 2, 3 depending on a number of (CuO₂)ₙ layers. In fact all these phases exhibit a certain variation of the cation ratio and the real composition can be different from the stoichiometric one.

A typical example is the first member of the series, (n = 1), which forms a relatively large homogeneity region of the pseudotetragonal solid solution (a ≈ b = 5.38 Å, c = 4.59 Å) lying outside the ideal composition Bi₂Sr₂CuO₆₊₈[1–9]. This solid solution (R) is formed by partial substitution of bismuth for strontium. In addition, if the excess of Bi (x) exceeds the deficit of Sr (y) in the general formula Bi₂₊ₓSr₂₋ₚCuOₓ₆₋ₘ, a part of Bi sites in -BiO- planes is probably occupied by copper [8, 9]. There is, however, a rather large discrepancy in the results of the individual authors as regards the stability of the solid solution. Very close to the nominal stoichiometry Bi₂Sr₂CuO₆ another phase (I) exists with the monoclinic C-centered symmetry and lattice parameters a = 24.451 Å, b = 5.425 Å, c = 21.95 Å, and β = 105.41° [1].
In this context it is evident that the investigation of the respective phase equilibria has the fundamental importance. Many authors devoted an attention to the sub-solidus region [2–10]. However, there is apparently little known about respective solid–liquid equilibria, although such knowledge has the essential importance for the growth of the single crystals. Therefore the present work was also devoted to the determination of the equilibria of the above mentioned phases with liquid. To estimate the evolution of these phase boundaries with increasing temperature the CuO–Bi$_2$SrO$_4$ pseudobinary phase diagram was also determined. Due to the wide spread of the experimental data concerning the determination of the thermodynamic stability region of the Bi$_{2+x}$Sr$_{2-y}$CuO$_{6+y}$ solid solutions a particular attention was devoted to the solution of this problem.

**Experimental techniques**

**Preparation of samples**

The samples of various composition were prepared by the usual mixing of the respective high purity powdered Bi$_2$O$_3$, SrCO$_3$, and CuO reagents at given ratios. The content of cation impurities being less than 0.01 weight% as well as the corrections for volatile impurities were determined by chemical analysis.

The samples used for the investigation of the equilibria in subsolidus region (single phase samples of Bi$_{2+x}$Sr$_{2-y}$CuO$_{6+y}$ and multi-phase samples of compositions in the vicinity of the homogeneity region) were calcined three times at the temperatures 760, 800, and 830°C for 24 h in each step. After the last calcination the mixtures were pressed into pellets of about 10 mm in diameter and 3 mm thick which were further heated for ~170 h at the temperature of the equilibrium studied, i.e. 850°C.

The precursors for the study of solid–liquid equilibria were calcined one time for 24 h at 725°C before pelletization. The final heat treatment was carried out repeatedly with an intermediate grinding at 750°C for the total time of 100 h. All procedures were performed in purified air.

**Differential thermal analysis**

Apparatus NETZSCH on line connected to computer and equipped by DDK measuring head with Pt-PtRh10 thermocouples and Pt crucibles was employed to determine the respective invariant points and liquidus curves. The temperature data were calibrated on the melting points of the well known metallic standards like Al, Ag, Au, Ni as well as on transition temperatures of ICTA standards.

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