**Phase Stability Domains of (Bi,Pb-2223): Data Sources,
Correlation, and Assessment***

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An assessment of the phase stability of lead-doped Bi-2223, (Bi,Pb)-2223, as a function of temperature and partial pressure of oxygen, $p(\text{O}_2)$, derived from equilibration and electromotive force studies carried out by numerous groups of investigators is presented. The data obtained from this assessment, coupled with additional more recent data from our laboratory, can be used to estimate the stability of this promising high- T_c bismuth cuprate system in the temperature range from 650 to 870°C and for oxygen partial pressures ranging from 10^{-5} to one atm.

1. INTRODUCTION

The phase relationships for the (Bi,Pb)-2223 system are more complex than those of YBCO and related 123 systems. Phase rule constraints make precise thermodynamic measurements difficult and hence complicate the task of rigorously defining the phase stability of (Bi,Pb)-2223. (Bi,Pb)-2223 is a solid solution phase, consequently, variation in cation ratios and oxygen content can affect the phase stability of this system as reported by various investigators. In this paper we have extended the assessment of Moon et al. [1] to include additional EMF measurements of Tetenbaum et al. [2,3] and recent equilibration measurements of Murphy and Dorris [4] carried out at ANL, as well as the results of other pertinent studies on this system reported in the literature.

2. RESULTS AND DISCUSSION

Figure 1 shows EMF and equilibration results obtained at ANL together with the results of Zhu and Nicholson [5], Daumling et al. (with and without Ag) [6], and Tallon et al. [7]. The measurements of Zhu and Nicholson [5], shown as solid lines in Fig. 1, have been chosen to serve as a reference phase diagram for comparison with the results of other studies. We believe that a portion of their phase diagram which we have represented by dotted lines may not be correct. From Fig. 1 it is seen that the EMF results of Tetenbaum et al. [2,3] in the temperature range 750-850°C are in reasonable agreement with the upper

phase boundary of Zhu and Nicholson [5], as well as the limited results of Daumling et al. [6], and Murphy and Dorris [4], which reflect the influence of silver on (Bi,Pb)-2223. At the lower phase boundary, the values derived from our EMF measurements lie close to the coexisting CuO/CuO₂ diphasic couple [8]. Based on the results of Murphy and Dorris [4], it is seen from Fig. 1 that silver shifts the decomposition temperature of (Bi,Pb)-2223 to lower values, as is also implied in the work of Daumling et al. [6] (see below).

The results of Zhu and Nicholson [5] (based on 120 h anneals in air) show that (Bi,Pb)-2223 coexists with Bi-2212 and Ca₂PbO₄-type phases at temperatures ranging from 800-840°C. Above 870°C, the superconductor decomposes to 2201 and an unknown phase. In the temperature range 700 to 840°C, (Bi,Pb)-2223 coexists with Ca₂PbO₄. At temperatures ranging from 820 to 840°C, the phases consist of (Bi,Pb)-2223 and 2201. However, at higher temperatures ranging from 850 to 870°C, only single-phase (Bi,Pb)-2223 is present. According to the measurements of Daumling et al. [6], for a given oxygen partial pressure, the (Bi,Pb)-2223 phase coexists with 2201 for temperatures above, and 2212 for temperatures below the stability regions as determined via XRD. The effect of silver is to lower the decomposition temperature for a given oxygen partial pressure by about 10 degrees. Based on EMF measurements, MacManus-Driscoll et al. [9] report that (Bi,Pb)-2223 decomposes to 2212, 2201, CaO, Cu₂O, and O₂ at temperatures less than 785°C and partial pressures of

oxygen ranging from about 10^{-5} to 10^{-4} atm. Above 785°C incongruent melting occurred yielding a liquid close in composition to 2212 and an alkaline earth cuprate of composition $(\text{Ca,Sr})_2\text{CuO}_3$. Silver was found to have little effect on the stability of the (Bi,Pb)-2223 phase in the temperature and pressure range investigated. Kusano et al. [10] reported precipitation of small particles of a phase with composition $\text{Sr}_{2.5}\text{Pb}_3\text{Ca}_2\text{CuO}_x$ when (Bi,Pb)-2223 was annealed in air below 830°C . When reheated in air at 850°C the precipitates dissolved into the (Bi,Pb)-2223 phase.

3. SUMMARY

Key findings of our assessment are that (1) the phase stability boundaries (for bulk (Bi,Pb)-2223) are reasonably well known based on data from several sources (the data for $\text{Ag}/(\text{Bi,Pb})$ -2223 is less comprehensive); (2) generally good agreement exists for $p\text{O}_2 = 0.075$ to 0.21 atm at temperatures between 810 and 850°C ; (3) proximity to silver, e.g., in silver-sheathed wire configurations, lowers the upper (temperature) stability boundary; (4) discrepancies in the data for bulk (Bi,Pb)-2223 exist at low $p\text{O}_2$ ($<10^{-2}$ atm) and low temperature ($<700^{\circ}\text{C}$).

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Figure 1. Phase stability boundaries for (Bi,Pb)-2223 as a function of temperature and oxygen partial pressure.