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THERMODYNAMIC AND NONSTOICHIOMETRIC BEHAVIOR OF THE LEAD-DOPED AND LEAD-FREE Bi-2212 SYSTEMS*

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DISCLAIMER

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Electromotive force (EMF) measurements of oxygen fugacities as a function of stoichiometry have been made on lead-doped and lead-free superconducting ceramics in the temperature range ~700-815°C by means of an oxygen titration technique. Equations for the variation of oxygen partial pressure with composition and temperature have been derived from our EMF measurements. Thermodynamic assessments of the partial molar quantities $\Delta\bar{H}(O_2)$ and $\Delta\bar{S}(O_2)$ for lead-doped Bi-2212 and lead-free Bi-2212 indicate that the solid-state decomposition of these bismuth cuprates at low oxygen partial pressure can be represented by the diphasic CuO-Cu_2O system. Comparison of these results with lead-doped Bi-2223 in powder and silver sheath form will be presented.

1. INTRODUCTION

The objective of our present studies is to investigate the phase stability and thermodynamic behavior of the lead-doped Bi-2212 and lead-free Bi-2212 systems as a function of oxygen partial pressure, oxygen stoichiometry, and temperature. In these studies the oxygen content was varied in well-defined small increments by means of a coulometric titration technique, and the equilibrium partial pressure (fugacity) above the sample was established from EMF measurements. This method is sensitive to detecting phase transformations, oxygen nonstoichiometry, and thermodynamic properties of bismuth-cuprate perovskites, where the single-phase homogeneity regions have a narrow range of composition. It should be emphasized that the complexity of the Bi-2212 system is further increased for practical considerations because the embodiment under current consideration for wire development consists of a silver-clad composite type conductor.

2. RESULTS AND DISCUSSION

A typical overview plot of the temperature dependencies of oxygen partial pressures for various oxygen coefficient values in the condensed phase of these bismuth cuprates derived from our EMF measurements [1] is shown in Figures 1 for lead-doped Bi-2212. Pertinent oxygen partial pressures are given above the horizontal lines in the figure. It is seen that cooling these bismuth cuprates at a fixed oxygen pressure increases the oxygen content of the condensed phase. The increase in flux-pinning and enhancement of J_c may be attributed (in part) to this increase in oxygen content of the condensed phase during slow cooling.

Equations for the variation of oxygen partial pressure with composition and temperature are given in Tables 1-2 for selected compositions. These equations can serve as a basis for the optimized preparation and subsequent behavior of these bismuth-cuprate materials when exposed to various oxygen partial pressures and temperatures.

In summary, key findings of our EMF measurements on the bismuth cuprates: lead-doped Bi-2212, lead-free Bi-2212, and lead-doped Bi-2223 systems are: (1) Single-phase homogeneity ranges of oxygen stoichiometry are very narrow compared to the well established $YBa_2Cu_3O_x$ system. (2) Solid-state decomposition of lead-free Bi-2212, lead-doped Bi-2212, and lead-doped Bi-2223 can all be represented by the diphasic CuO-Cu_2O system. (3) Oxygen content of these bismuth cuprates increases with decreasing temperature at constant oxygen partial pressure. (4) In accord with our EMF measurements on lead-doped Bi-2223, it was found that lead-doped Bi-2223 in a silver sheath is stable at 815°C for oxygen pressures between 0.02 and 0.13 atm.[2]

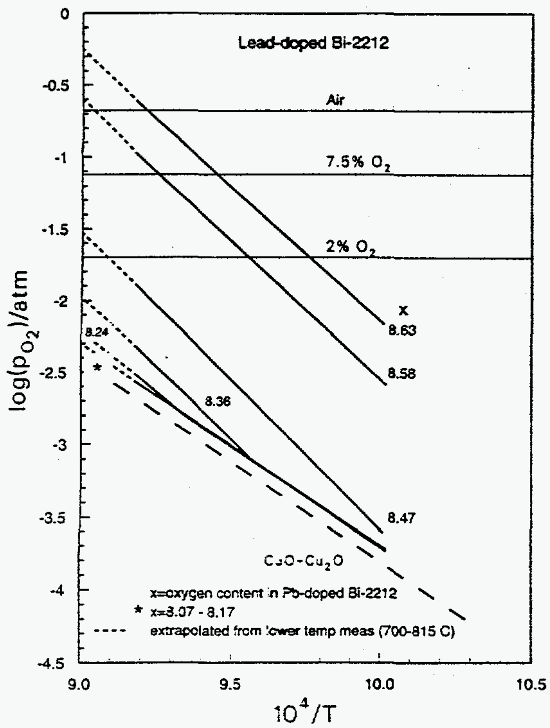

Fig. 1. Overview plot of variation of oxygen pressure with oxygen stoichiometry and temperature.

References

1.) M. Tetenbaum and V.A. Maroni, Physica C 260 (1996) 71.
2.) M. Tetenbaum, M. Hash, B.S. Tani, J.-S. Luo, and V.A. Maroni, Physica C 249 (1995) 396.

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Table 1. Lead-doped Bi-2212 system.

Log P (O_2)/atm = A/T (K) + B

Oxygen content	A	B	Temperature range, °C	
8.63	−18730	16.6	725 - 815	
8.58	−19500	16.9	725 - 815	
8.47	−20650	17.1	725 - 815	
8.36	−20200	16.2	770 - 815	upper slope
8.36	−14000	10.1	725 - 770	lower slope
8.32	−20130	16.0	790 - 815	upper slope
8.32	−13900	10.2	725 - 790	lower slope
8.24	−19560	15.5	800 - 815	upper slope
8.24	−13600	9.9	725 - 800	lower slope
8.17	−13810	10.1	725 - 815	
8.01	−13810	10.1	725 - 815	
CuO - Cu_2O	−13700	9.9	725 - 815	pure phases

Table 2. Lead-free Bi-2212 system.

Log P (O_2)/atm = A/T (K) + B

Oxygen content	A	B	Temperature range, °C	
7.77	−16330	14.3	725 - 815	upper slope
7.77	−20170	18.2	710 - 725	lower slope
7.73	−19990	16.9	700 - 815	
7.65	−19580	15.9	730 - 815	upper slope
7.65	−13590	9.90	700 - 815	lower slope
7.59	−20250	16.4	750 - 815	upper slope
7.59	−13880	10.2	700 - 750	lower slope
7.52	−17540	13.7	775 - 815	upper slope
7.52	−13830	10.2	700 - 775	lower slope
7.41	−13860	10.2	700 - 815	
7.01	−13680	10.0	700 - 815	
CuO - Cu_2O	−13700	9.9	700 - 815	pure phases