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| <b>Project Title:</b>   | <b>Phase Relations of High <math>T_c</math> Superconductors</b> |
| <b>Organization(s):</b> | <b>NIST, Ceramics Division, Gaithersburg, MD 20899</b>          |
| <b>Presenters:</b>      | W. Wong-Ng and L.P. Cook  |
| <b>FY 2004 Funding:</b> | \$250 K   |

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**Project Purpose and FY 2004 Objectives:** Our principal 2004 project objective is to develop a critical phase equilibrium database for Ba-R-Cu-O (R=Y, lanthanides) second generation RABiTS and IBAD coated conductor applications. In addition to phase diagram studies of the Ba-R-Cu-O systems, subprojects include phase transformation determination of  $Ba_2RCu_3O_{6+x}$  (213), and characterization of the “*ex-situ*  $BaF_2$  process” of  $Ba_2YCu_3O_{6+x}$  (Y-213) formation. To investigate the interplay of phase equilibria and kinetics in the Ba-Y-Cu-O-OH system, we have collaborated with ORNL, ASC and BNL to determine the occurrence of melt in association with the defluorination process, and to follow the phase formation of the Y-123 phase in precursor films using high temperature x-ray diffraction (HTXRD). An understanding of the interfacial reaction of Y-213 phases with the buffer layers is critical to the development of coated conductor tapes. Consequently, another objective is to collaborate with ORNL and LANL to investigate the phase equilibria of the multicomponent systems representing the interaction of  $Ba_2YCu_3O_{6+x}$  with selected buffer materials. Additionally, by mixing a small lanthanide ion with larger R in R-213 solid solutions, flux-pinning and melting properties can be tailored and optimized. In collaboration with LANL and the AFRL at Wright-Patterson (AFRL-WP), we continued to characterize the high  $T_c$  mixed lanthanide solid solutions, including flux-pinning studies. Finally, in order to provide thermodynamic data for the challenging Mg-B system, we continued to pursue both experimental and theoretical studies of  $MgB_2$ .

**FY 2004 Performance and FY 2005 Plans:** An advisory team for our phase equilibria research activities was formed to ensure relevancy, efficiency, and impact of our work. Based on various interactions with the team members, we have continually refined our FY 2004 objectives. We have successfully applied our experimental procedure and specialized apparatus to construct phase diagrams of the Ba-Gd-Cu-O, Ba-Dy-Cu-O and Ba-Yb-Cu-O systems under controlled atmosphere conditions. In collaboration with BNL and Caltech, an understanding of the trend of orthorhombic to tetragonal phase transformation temperature was obtained. We have investigated the solid solution range of the  $Ba_{2-x}(R,Y)_{1+x}Cu_3O_z$  phase, where R= Sm, Eu and Gd. This year we have also successfully constructed a steam furnace for controlling water vapor pressure, an important step in our investigation of the role of  $Ba(OH)_2$ -related liquid in low-temperature melting of the Ba-Y-Cu-O-OH system. In collaboration with ORNL, we have made significant progress in understanding the mechanism of phase evolution of the  $BaF_2$  films (prepared using both e-beam evaporation and TFA methods) by a combined use of HTXRD and TEM. In collaboration with LANL and ORNL, we continued to study the phase equilibria of the multicomponent systems representing the interaction of  $Ba_2YCu_3O_{6+x}$  with  $CeO_2$  and  $SrTiO_3$  buffer materials.

The FY 2005 plan builds upon FY2004 progress. We will continue our interactions with the ‘phase equilibria advisory team’, and our collaborations with ORNL, ASC, and BNL on the the  $BaF_2$  subproject, with LANL and AFRL-WP on the mixed-lanthanides subproject, and with ORNL and LANL on superconductor/buffer interaction subproject. We will also continue to study phase equilibria of the Ba-R-Cu-O systems under reduced oxygen pressures. For the  $BaF_2$  project, emphasis will continue to be placed on both modeling and experimental work related to melting equilibria in the multicomponent Ba-Y-Cu-O-F-OH system and pertinent subsystems. In collaboration with ORNL, we will use combined HTXRD and TEM to compare the mechanism of phase evolution of the R-213 superconductor films as a function of different stoichiometries. These films will be prepared using both e-beam and TFA methods.

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**FY 2004 Results:** Key results from the FY 2004 program are summarized below:

- 1) The phase diagrams of the Ba-R-Cu-O (R=Gd, Dy and Yb) systems in 0.1 % O<sub>2</sub> have been constructed and compared with other members of the Ba-R-Cu-O systems. A trend in the diagrams was observed.
- 2) The Ba<sub>2-x</sub>(R, Y)1+xCu<sub>3</sub>O<sub>z</sub> systems (R=Sm, Eu and Gd) have been characterized. The size of the solid solution region varies with the oxygen partial pressure as well as the size of R (with AFRL-WP and LANL).
- 3) The phase formation mechanism of Y-213 during the “BaF<sub>2</sub> process” was determined to depend on precursor type (i.e., Y<sub>2</sub>O<sub>3</sub> vs YF<sub>3</sub>), as well as precursor stoichiometry. A barium oxyfluoride superlattice phase was confirmed to be involved in the phase formation process (with ORNL).
- 4) Further studies confirmed earlier evidence of low-temperature melts in the F-rich region of the Ba,Y,Cu//O,F reciprocal system. Phase equilibria of the intermediate BaF<sub>2</sub>-CuF<sub>3</sub>-YF<sub>3</sub>-CuO<sub>x</sub> region was successfully studied. The low temperature DTA event occurring in this region was determined to be due to a solid state phase transition in yttrium oxyfluoride.
- 5) Phase diagrams of the Ba-Y-Cu-O-F-OH binary systems, including Ba(OH)<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>, Ba(OH)<sub>2</sub>-CuO, Ba(OH)<sub>2</sub>-BaO, and BaF<sub>2</sub>-BaO, have been initiated using a specially constructed vapor pressure furnace.
- 6) Phase equilibria for pseudobinary systems of Ba<sub>2</sub>YCu<sub>3</sub>O<sub>6+x</sub> with buffer materials CeO<sub>2</sub> and SrTiO<sub>3</sub>, together with selected subsystems, were determined (with LANL).
- 7) The orthorhombic to tetragonal phase transition temperature of Ba<sub>2</sub>RCu<sub>3</sub>O<sub>6+x</sub> was characterized and successfully modeled (with BNL and Caltech). The observation that the smaller the ionic radius of R, the higher the transition temperature, was found to be related to the effect of strain.
- 8) Study of the effect of Ba<sub>2</sub>CuO<sub>5</sub> on the superconducting properties of 213-films was initiated (with AFRL-WP).
- 9) Enthalpy of formation and vapor pressure of oxygen-free MgB<sub>2</sub> were determined (with Ames Lab).

**Technology Integration:** To ensure the relevance of our phase equilibrium studies, we work closely with other national laboratories, with universities, and with industry. We have formed a “phase equilibrium advisory team” which includes members from the superconductor industry, government laboratories and universities: ASC, IGC, Oxford Instruments, ORNL, LANL, BNL, AFRL-WP, Columbia University, and University of Houston. We are currently collaborating on the BaF<sub>2</sub> project with ORNL, ASC, and BNL, and with other scientists of the NIST Ceramics and Metallurgy Divisions and the Center for Neutron Research. We are collaborating with LANL and AFRL-WP on the mixed lanthanide projects, with ORNL and LANL on study of interaction of Y-213 with buffers, with Florida State University on a phase equilibria study of Pb-free 2223, with BNL and Caltech on phase transformations of R-213, and with Ames Lab on MgB<sub>2</sub> studies.