
Project Title:	Phase Equilibrium Relations of High T_c Superconductors
Organization(s):	NIST, Ceramics Division, Gaithersburg, MD 20899
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Project Purpose and FY 2003 Objectives: The overall objective of this project is to develop a critical database for phase diagrams for the Ba-R-Cu-O (R=Y and lanthanides) second generation RABiTS and IBAD coated conductor applications. To build the database, we continue to systematically study the phase diagrams of the Ba-R-Cu-O systems. By mixing a small lanthanide ion with Ba_{2-x}Nd_{1+x}Cu₃O_z (With-123) solid solution, both flux-pinning and melting properties can be tailored and optimized. In collaboration with Los Alamos Laboratory (LAL) and the Air Force Laboratory at Wright-Patterson (AFL), we continued to characterize the mixed lanthanide Ba_{2-x}(R,R')_{1+x}Cu₃O_z solid solutions. Another important objective of our investigation is to provide basic equilibrium data for the *ex-situ* BaF₂ processing of Y-123. As the interplay of phase equilibria and kinetics is important in this system, we have collaborated with Oak Ridge National laboratory (ORNL), and Brookhaven National Laboratory (BNL) to investigate the occurrence of melt in association with the defluorination process, and to follow the phase formation of the Y-123 phase of the □ctivitie films using high temperature x-ray diffraction (HTXRD). The understanding of the interfacial reaction of Y-213 phases with the buffer layers is critical to the development of the coated conductor tapes. We have initiated an effort on the multicomponent system representing the interaction of Ba₂YCu₃O_{6+x} with CeO₂. Other research □ctivities during FY2003 pertain to the recently-discovered high T_c material, MgB₂. Our experimental approach in the MgB₂ system is focused on determining thermodynamic propterties, which may be used to extend direct experimental measurements in this system.

FY 2003 Performance and FY 2004 Plans: Significant progress has been made towards each of our objectives during FY 2003. We have successfully applied our experimental procedure and specialized apparatus to construct phase diagrams of the Ba-Gd-Cu-O, Ba-Eu-Cu-O, and Ba-Ho-Cu-O systems under controlled atmosphere conditions. We have investigated the solid solution range of the Ba_{2-x}(Nd,R)_{1+x}Cu₃O_z phase, where R= Gd; and Ba_{2-x}(R,Y)_{1+x}Cu₃O_z, where R=Eu and Gd. Previously, we initiated the systematic investigation of the phase equilibria of the Ba-Y-Cu-O system with BaF₂ and H₂O, and the possible role of hydroxide in participating in the low-temeprature melts. This year we investigated phase equilibrium details in the Ba,Y,Cu//O,F subsystems (BaO-Y₂O₃-CuO_x-BaF₂, BaF₂-Y₂O₃-CuO_x-YF₃ and selected pseudo-binaries and ternaries) to search for low-melting regions, and continue to study the possible involvement of hydroxides. Our setup of a position sensitive detector on our HTXRD diffractometer allows for efficient study of Ba-Y-Cu-F films under atmospherically-controlled conditions and in the presence of water.

The FY 2004 plan is based upon this progress. We will continue our collaborations with ORNL, and BNL on the the BaF₂ project, LANL and AFL on the mixed-lanthanides project. We will continue to study phase equilibria of the Ba-R-Cu-O systems under reduced atmosphere conditions. For the BaF₂ project, emphasis will be placed on both modeling and experimental work of the melting equilibria of the multicomponent Ba-Y-Cu-O-F-OH system and pertinent subsystems. We will continue to investigate the mechanism of phase evolution of the Y-213 superconductor using HTXRD, and the interaction of the BYC phase with various potential substrate materials.

FY 2003 Results: Key results from the FY 2003 program are summarized below:

1. The phase diagrams of the Ba-R-Cu-O (R=Eu, Ho) systems in 0.1 % O₂ have been constructed. No significant solid solution for Eu-213 was found (x≤0.1). Ba₄R₂Cu₂O_x, which is present in the R=Nd and Sm systems is absent here. The solid solution range of (Ba,Eu)₂CuO_{3+x} is smaller than that in the Nd- and Sm-analogs. The phase diagram of the Ba-Ho-Cu-O system under 0.1% is very similar to the Y-analog. No solid solution was observed. Phase compatibilities among the four critical phases (Ba:Er:Cu) 213, 413, BaCuO_{2+x}, and BaHo₂CuO₅ are different from those reported in the literature.
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2. In collaboration with Los Alamos Laboratory and the Air Force Laboratory at Wright-Patterson, study of the $Ba_{2-x}(Nd, Gd)_{1+x}Cu_3O_z$ and $Ba_{2-x}(Gd, Y)_{1+x}Cu_3O_z$ systems were completed and the study of the $Ba_{2-x}(Eu, Y)_{1+x}Cu_3O_z$ system has been initiated to determine the single-phase solid solution region. The size of this solid region was found to be larger than that of the $Ba_{2-x}(Gd, Y)_{1+x}Cu_3O_z$ system.
 3. Phase equilibria of the $BaF_2-CuF_3-YF_3-CuO_x$ region in the Ba, Y, Cu//O, F reciprocal system was successfully studied. The low temperature DTA event occur in this region was determined to be due to the phase transformation of a yttrium oxyfluoride phase. Further studies also confirmed earlier evidence of low-temperature melts in the F-rich $BaF_2-YF_3-CuF_2-CuO_x$ region, at temperatures below 600 °C.
 4. Phase diagrams of the binary systems $BaF_2-Y_2O_3$, $BaO-BaF_2$, BaF_2-CuO , and BaF_2-Cu_2O have been studied by DTA/TGA and quenching. These results emphasize the importance of p_{O_2} in oxyfluoride melting reactions.
 5. Experiments and thermochemical calculations on the stability of hydroxides have been conducted to show their possible role in the low temperature region.
 6. HTXRD was successfully applied to a number of ORNL prepared films in the representative binary systems of the Ba, Y, Cu//O, F reciprocal system. Phase formation of binary and ternary systems were obtained which is critical to the understanding of phase formation of the Y-213 superconductor. Combined TEM/HTXRD results identified key phases during the phase evolution.
 7. We have determined the phase diagram of the pseudo-binary system $Ba_2YCu_3O_{6+x} - CeO_2$. Phase diagram study of the multicomponent $BaO-Y_2O_3-CeO_2-CuO_x$ has been initiated. In the $BaO-Y_2O_3-CeO_2$ subsystem, $Ba(Ce, Y)O_x$ and $(Ce, Y)O_x$ solid solutions were identified.
 8. We have successfully measured enthalpy of formation of MgB_2 on several additional samples at 298K by solution calorimetry. Results indicate the importance of atmospheric influence on the measured properties. The vapor pressure of MgB_2 at low pressures was measured using Knudsen effusion vacuum thermogravimetry; these results can be compared with earlier results at 0.1 MPa total pressure.

Research Integration: To ensure the relevance of our phase equilibrium studies, we work closely with other national laboratories, with universities, and with industry. We are currently collaborating on the BaF_2 project with Oak Ridge National laboratory and Brookhaven National Laboratory, and with other scientists of the NIST Ceramics, Metallurgy Divisions and the Center for Neutron Research. We are collaborating with Los Alamos National Laboratory and the Airforce Laboratory (Wright-Paterson) on the mixed lanthanide projects, and with University of Wisconsin and Florida State University on BSCCO. Continuous interactions and exchanges of information are maintained with American Superconductor, Brookhaven National Laboratory, the Naval Research Laboratory, University of Houston, and the US Airforce at Wright-Patterson.
