

## Coated Conductors: Phase Relations in the Ba-Y-Cu-F-O-H System

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### INTRODUCTION

E-beam co-evaporated BaF<sub>2</sub>-Y-Cu-precursor films on rolling-assisted-biaxially-textured-substrate (RABiTS), post-annealed in the presence of water vapor (“BaF<sub>2</sub> *ex situ* process”) have demonstrated the potential of producing high quality, long length Ba<sub>2</sub>YCu<sub>3</sub>O<sub>6+x</sub> (Y-213) superconductors [1]. The details of phase equilibria and phase evolution of the Y-213 phase in the multi-component Ba-Y-Cu-F-O-H system have been the subject of intensive investigation in recent years. It is crucial to determine the role of liquid, specifically, whether an intermediate low-temperature liquid forms, and, whether its formation plays a role in the formation of the Y-213 phase. We have completed thermal analysis studies in the model system Ba,Y,Cu//O,F to determine the lowest melting temperatures. We have also employed *in situ* high temperature x-ray diffraction (HTXRD) and high resolution transmission electron microscopy (HRTEM) to follow the phase formation of Y-213, starting from amorphous films prepared at ORNL.

### EXPERIMENTAL<sup>1</sup>

#### (1) Phase Evolution

The “BaF<sub>2</sub>” precursor films were prepared by e-beam evaporation of Cu and Y metal and BaF<sub>2</sub> at room-temperature on model (100) SrTiO<sub>3</sub> substrates [1]. Four sets of films used for this study included precursor phases of: (1) BaF<sub>2</sub>, Cu and Y; (2) BaF<sub>2</sub> and Cu; (3) BaF<sub>2</sub> and Y; and (4) BaF<sub>2</sub>. A high-temperature Siemens 5000  $\theta$ - $\theta$  geometry X-ray diffractometer equipped with both a scintillation counter detector and a position sensitive detector (PSD) was modified for the present study by adding a gas flow apparatus. This apparatus included a series of bubblers containing NaCl-saturated water at room temperature, and an oxygen analyzer. Helium gas containing  $\approx 1000$  ppm O<sub>2</sub> by volume was flowed through the bubblers and passed directly over the sample in the enclosed furnace chamber. High-resolution imaging of selected samples was performed in a JEOL 3010 UHR TEM operated at 300 kV.

#### (2) Melting in the Ba-Y-Cu//O,F system

Several of the components of the Ba,Y,Cu//O,F system, most notably BaO and CuF<sub>2</sub>, are atmospherically sensitive, and so all materials were handled under glove box conditions in an argon atmosphere. BaO was prepared from BaCO<sub>3</sub> by vacuum decomposition. All materials were weighed as fine powders and thoroughly mixed repeatedly with a mortar and pestle. Platinum was selected as the best compromise for the container material under the conditions of our experiments. Differential thermal analysis (DTA) experiments were carried out on samples using an electronically upgraded Mettler TA1 system enclosed in an argon-filled glovebox.

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<sup>1</sup>Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by NIST, nor is it intended to imply that the materials/equipment identified are necessarily the best available for the purpose.

## RESULTS AND DISCUSSION

### (1) Phase evolution

Figure 1 shows the x-ray patterns of a representative amorphous BaF<sub>2</sub>-Y-Cu film. A sequence of phase evolution is observed. For example, BaF<sub>2</sub>-type oxyfluoride and CuO phases crystallize around 300 °C. At 550 °C, Cu<sub>2</sub>O converts to CuO. At 700 °C, both Y<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub> and an unknown phase having a strong reflection at 25° appear, along with a small amount of Y-213. The unknown phase disappeared after about 75 minutes at 735 °C, and the Ba(O,F)-based phase disappeared after 100 minutes, while the Y-213 continues to grow. To quench the unknown phase, we used another film and stopped the experiment after 30 minutes at 735 °C. The HRTEM image revealed a coherent region of BaF<sub>2</sub>-based superstructure (pseudo-orthorhombic cell with  $a=7.4$  Å,  $b=10.5$  Å ([2])) that can explain the x-ray reflections in question. A systematic HTXRD studies of the subsystems BaF<sub>2</sub> + Y, BaF<sub>2</sub>+Cu+ H<sub>2</sub>O, and BaF<sub>2</sub> indicated that the superlattice develops in each of these systems, including pure BaF<sub>2</sub>, and therefore its formation cannot be explained by cation (e.g. Ba/Y) ordering. Most likely, the superstructure is related to the ordering of anions and/or vacancies.

In general, the *ex-situ* BaF<sub>2</sub> process involves a hydration/oxidation reaction at 735 °C:  
 $(2 \text{ BaF}_2 + \text{ Y} + 3 \text{ Cu})_{\text{amorphous}} + 2 \text{ H}_2\text{O} + (4.5 + x)/2 \text{ O}_2 \rightarrow \text{ Ba}_2\text{YCu}_3\text{O}_{6.5+x} + 4\text{HF(g)}$ . Based on HTXRD experiments, the conversion process of the films can be expressed as a sum of several intermediate steps, including reaction between precursor components and O<sub>2</sub> to form oxides, and BaF<sub>2</sub> with water vapor to form Ba-O-F (barium fluoride-based oxyfluoride and superstructure). Ba-O-F phases then react with Y<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub>, CuO and water vapor to form the Y-213 phase.

### (2) Melting in the Ba-Y-Cu//O,F system

The Ba-Y-Cu//O,F system was modeled in compositional space as a trigonal prism (Fig. 2), which can be viewed as consisting of three tetrahedra (BaO-Y<sub>2</sub>O<sub>3</sub>-CuO<sub>x</sub>-BaF<sub>2</sub>, BaF<sub>2</sub>-YF<sub>3</sub>-CuF<sub>2</sub>-CuO<sub>x</sub>, and BaF<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>-CuO<sub>x</sub>-YF<sub>3</sub>) [3]. In the fluorine-rich BaF<sub>2</sub>-YF<sub>3</sub>-CuF<sub>2</sub>-CuO<sub>x</sub> system, low-temperature melts were determined by DTA to occur below 600 °C. A systematic study of samples in the BaF<sub>2</sub>-YF<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-CuO<sub>x</sub> subsystem showed low temperature DTA events at 500 °C-600 °C. However, a combined high temperature X-ray and neutron diffraction study showed this event to be due to a non-quenchable phase transformation of the YOF phase (from low-temperature rhombohedral to high-temperature cubic). All regions in this subsystem have high melting temperatures (> 900 °C). In the BaO-Y<sub>2</sub>O<sub>3</sub>-CuO<sub>x</sub>-BaF<sub>2</sub> subsystem, we systematically explored the eutectic melting region in Ba-Y-Cu-O as a function of p<sub>O2</sub>. Experiments were performed on samples without H<sub>2</sub>O or BaF<sub>2</sub> (from 100 % oxygen to 0.02 % oxygen, by volume), and with the presence of both H<sub>2</sub>O and BaF<sub>2</sub>. It was found that even with the presence of both BaF<sub>2</sub> and H<sub>2</sub>O, the lowest melting temperature was about 815 °C at 0.02 % O<sub>2</sub>, which is substantially higher than 735 °C (tape processing temperature). Apparently, low-melting liquids do not appear as stable phases in the BaO-Y<sub>2</sub>O<sub>3</sub>-CuO<sub>x</sub>-BaF<sub>2</sub> subsystem under the experimental conditions described, although the possibility of metastable liquids cannot be ruled out. It is also possible that Ba(OH)<sub>2</sub> is involved in producing a low melting liquid.

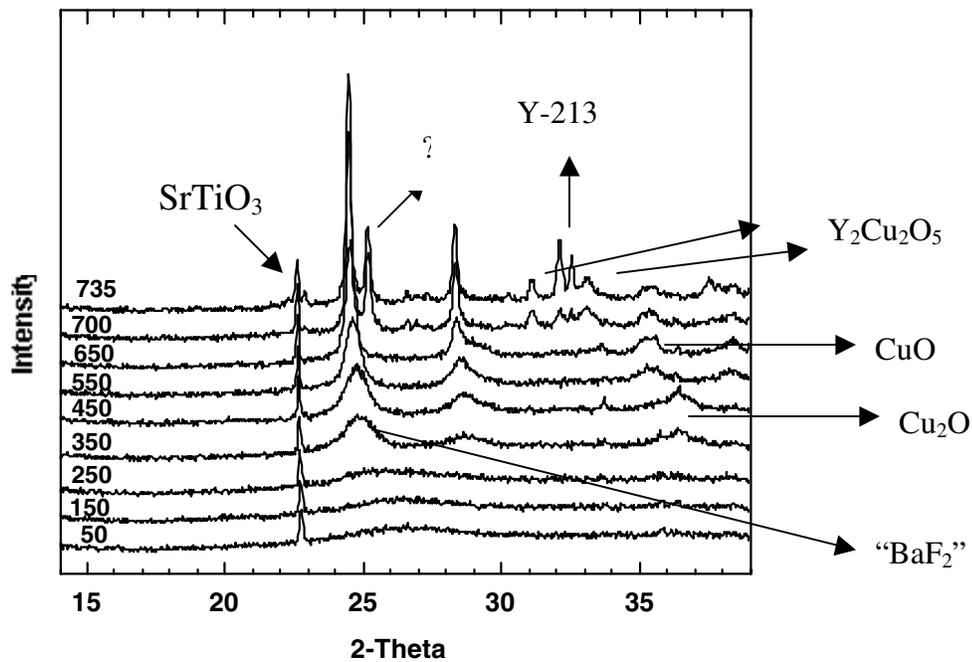


Fig. 1. X-ray diffraction patterns of a BaF<sub>2</sub>-Y-Cu film as a function of temperature (°C).

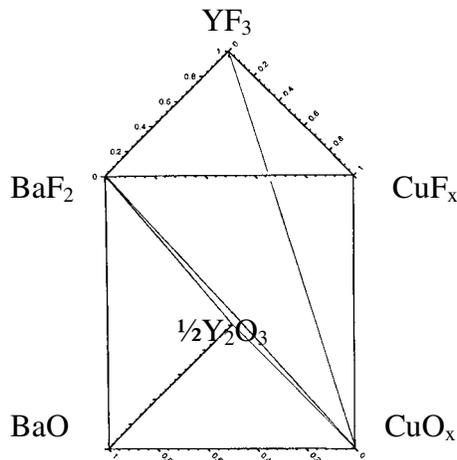


Fig.2. Triangular prism representing the Ba,Y,Cu/F,O system

## REFERENCES

1. R. Feenstra, T. B. Lindemer, J. D. Budai, and M. D. Galloway, *J. Appl. Phys.* **69**, 6569 (1991).
2. L. Wu, Y. Zhu, V.F. Solovyov, H.J. Wiesmann, A.R. Moodenbaugh, R.L. Sabatini, and M. Suenaga, *J. Mater. Res.* **16** [10] 2869 (2001).
3. W. Wong-Ng, L.P. Cook, *Materials for High-Temperature Superconductor Technologies*, Materials Research Society Symposium Proceedings, **689**, Eds. Paranthaman et. al.; Nov. 26-29, 2001, Boston, MA; Materials Research Society, Warrendale, PA 15086, pp. 337 (2002).