

## MICROGRAVITY PROCESSING OF OXIDE SUPERCONDUCTORS

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### Introduction

Considerable effort has been concentrated on the synthesis and characterization of high  $T_c$  oxide superconducting materials. The YBaCuO system has received the most intense study, as this material has shown promise for the application of both thin film and bulk materials. There are many problems with the application of bulk materials; weak links, poor connectivity, small coherence length, oxygen content and control, environmental reactivity, phase stability, incongruent melting behavior, grain boundary contamination, brittle mechanical behavior, and flux creep. The extent to which these problems are intrinsic or associated with processing is the subject of controversy. This study seeks to understand solidification processing of these materials, and to use this knowledge for alternative processing strategies, which, at the very least, will improve the understanding of bulk material properties and deficiencies.

In general, the phase diagram studies of the YBaCuO system have concentrated on solid state reactions and on the  $Y_2BaCuO_x + \text{liquid} \rightarrow YBa_2Cu_3O_{7-8}$  peritectic reaction. Little information is available on the complete melting relations, undercooling, and solidification behavior of these materials. In addition, rare earth substitutions such as Nd and Gd affect the liquidus and phase relations<sup>1</sup>. These materials have promising applications, but lack of information on the high temperature phase relations has hampered research. In general, the understanding of undercooling and solidification of high temperature oxide systems lags behind the science of these phenomena in metallic systems. Therefore, this research investigates the fundamental melting relations, undercooling, and solidification behavior of oxide superconductors with an emphasis on improving ground based synthesis of these materials.

### Experimental Results

Significant progress has been made in understanding the above mentioned phenomena. Two techniques of containerless processing were utilized, Aero-Acoustic Levitation and drop tube processing. The liquidus of the  $YBa_2Cu_3O_{7-8}$  has been determined to be 1820 °C, a considerably higher temperature than reported in the literature<sup>2,3</sup>. In addition, deep undercooling of these materials has been accomplished. In many cases tetragonal  $REBa_2Cu_3O_x$  was solidified directly from the melt, demonstrating that formation of the intermediate phases in these systems can be avoided by melt processing and undercooling.

Aero-Acoustic Levitation (AAL) experiments provided a means for direct observation of large (2.5 mm) samples during processing<sup>4</sup>. The Ultra High Speed Thermal Imaging (UHSTI) system developed at Vanderbilt has proven to be useful for obtaining spatial thermal information during melting and solidification. Upon rapid solidification, several thermal events were observed, most

notably a low temperature (~1080 K) slow moving event which led to a cellular structure with tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_x$  being the primary solidification phase. When full melting of the sample was obtained, single phase tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_x$  was formed upon recalescence<sup>5</sup>.

Drop tube experiments at Vanderbilt University have concentrated on determining the high temperature phase relations in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ ,  $\text{NdBa}_2\text{Cu}_3\text{O}_x$ , and partial substitutions of Nd for Y. These experiments involved melting small powders (50 - 100  $\mu\text{m}$ ) in a pure oxygen environment using a 2 meter drop tube. Melted powders solidified in free fall. The resulting samples were examined microstructurally using scanning electron microscopy, energy dispersive spectroscopy (EDS) and optical microscopy. Powder x-ray diffraction was performed for phase identification. Because these materials possess a low thermal conductivity, the smallest resultant samples were used for comparison based on the fact that they were more likely to reach the furnace temperature during free fall. Table 1 lists the compositions processed and the ranges of processing temperatures in these experiments. Experiments were performed at 25 ° increments within each range.

<i>Sample Material</i>	<i>Temp. (°C)</i>
$\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$	1650-1800
$\text{Y}_{.9}\text{Nd}_{.1}\text{Ba}_2\text{Cu}_3\text{O}_x$	1650-1800
$\text{Y}_{.8}\text{Nd}_{.2}\text{Ba}_2\text{Cu}_3\text{O}_x$	1650-1800
$\text{Y}_{.7}\text{Nd}_{.3}\text{Ba}_2\text{Cu}_3\text{O}_x$	1575-1800
$\text{Y}_{.5}\text{Nd}_{.5}\text{Ba}_2\text{Cu}_3\text{O}_x$	1525-1800
$\text{Y}_{.3}\text{Nd}_{.7}\text{Ba}_2\text{Cu}_3\text{O}_x$	1475-1800
$\text{Y}_{.1}\text{Nd}_{.9}\text{Ba}_2\text{Cu}_3\text{O}_x$	1450-1800
$\text{NdBa}_2\text{Cu}_3\text{O}_x$	1400-1800

**Table 1.** Drop Tube Experiments Performed.

Microstructural analysis using energy dispersive spectroscopy along with powder X-ray diffraction on the resultant samples provides for developing a clear picture of the phases that solidify. Figure 1 summarizes these analyses for all of the drop tube experiments which have been performed in this study. The lines indicate the primary solidification phase as a function of composition and drop tube processing temperature. At processing temperatures above the solid line, the samples were completely molten, then undercooled to below the RE-1:2:3 peritectic to solidify single phase tetragonal RE-1:2:3 from the melt. Below this line the existence of facted, high temperature phases indicates that the samples were processed in a solid + liquid region of the phase diagram. Therefore, this line defines the liquidus between pure Y-1:2:3 and Nd-1:2:3. The data show a decreasing trend in the liquidus with increasing Nd to and including the composition  $\text{Y}_{.1}\text{Nd}_{.9}\text{Ba}_2\text{Cu}_3\text{O}_x$ . At that composition, the liquidus temperature reaches a minimum of 1500 °C ( $\pm 25$  °C). For the pure Nd-1:2:3 samples, the liquidus increases markedly to 1600 °C ( $\pm 25$  °C).

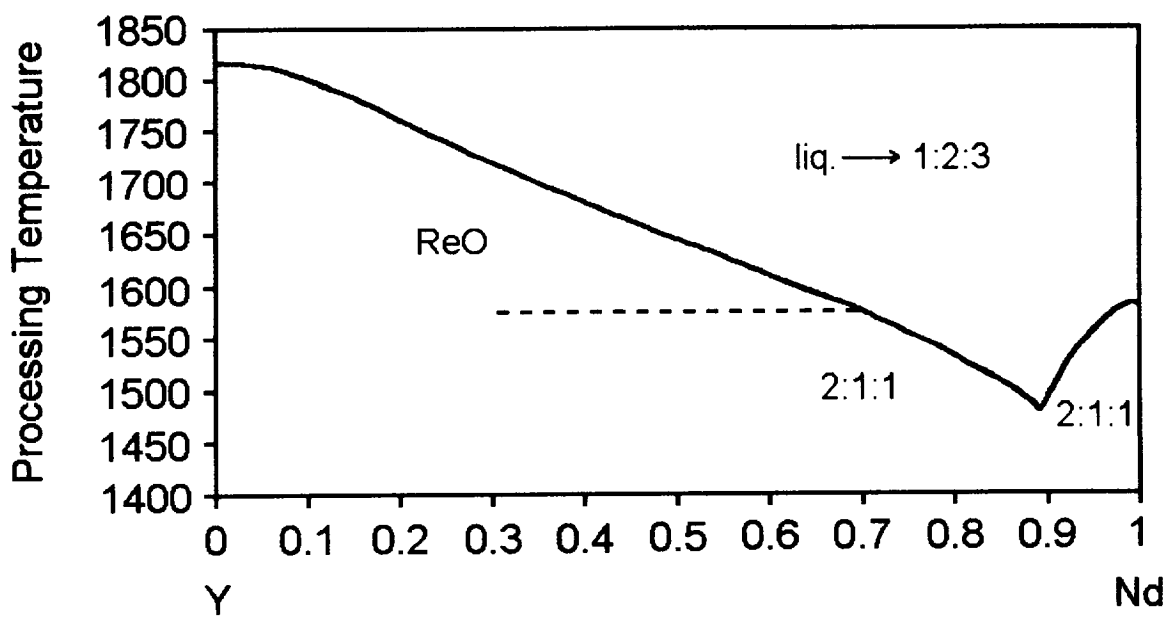


Figure 1. Schematic diagram of Nd atoms/unit cell vs. drop tube processing temperature showing the primary solidification phase. Phases are as follows: 2:1:1 =  $Y_2BaCuO_5$ , ReO = Rare earth oxide, 1:2:3 = tetragonal  $RE_{1(Y+Nd)}Ba_2Cu_3O_x$ .

A typical micrograph from a sample that did not melt completely is shown in figure 2. This result is from a sample of pure  $YBa_2Cu_3O_{7-8}$  processed at 1775 °C. Here, four distinct phases can be seen. Particles of  $Y_2O_3$  (dark gray) are seen accompanied by dendrites of the darkest phase. The darkest phase corresponds to  $Y_2BaCuO_5$ . The surrounding matrix is eutectic in nature and is composed of at least two different Ba Cu oxide phases. This morphology appears frequently when samples are not completely molten prior to solidification. In this case, samples reached temperatures within the  $Y_2O_3$  + liquid region of the phase diagram. Once they passed out of the hot zone and began cooling, the  $Y_2BaCuO_5$  phase nucleated on the surfaces of these particles. Upon further cooling, the remaining liquid solidified as a Ba Cu oxide eutectic.

Figure 3 shows a sample of  $Y_{.8}Nd_{.2}Ba_2Cu_3O_x$  processed at 1775 °C in the drop tube. Here, tiny feathery dendrites of  $Y_2BaCuO_5$  are observed within a matrix of Ba Cu oxides. In this case, the sample was nearly, but not completely molten in free fall. Enough solid  $RE_2O_3$  remained to nucleate  $Y_2BaCuO_5$ . Figure 4 shows a sample of  $Y_{.3}Nd_{.7}Ba_2Cu_3O_x$  processed at 1675 °C where large dendrites and grains of pure  $Y_{.3}Nd_{.7}Ba_2Cu_3O_x$  formed. Microstructures of this type are an indication that the samples were completely molten prior to solidification. Upon cooling, samples undercooled to below the  $Y_{.3}Nd_{.7}Ba_2Cu_3O_x$  peritectic and solidified tetragonal 1:2:3 phase directly from the melt.

Nd substitution affects phase selection in the following ways. First, as the Nd content increases, the tendency for the formation of RE oxide from the melt decreases. At a Nd content of 0.7 atoms/unit cell, RE oxide does not appear in the resultant samples. Secondly, for intermediate

compositions ( $0.5 \geq x \geq 0.3$ ), the 2:2:3 phase exists at high temperatures. This phase is previously unreported and occurs only in the presence of 1:2:3. Figure 5 is a micrograph of a  $Y_{.5}Nd_{.5}Ba_2Cu_3O_x$  sample processed at 1725 °C where the 2:2:3 phase appears between large grains of  $RE_1Ba_2Cu_3O_x$ .

The decreasing tendency for RE oxide to form and the overall lowering of the liquidus with increasing Nd content additionally alters phase selection in that the RE-1:2:3 phase forms more readily. This is coupled with a decrease in the number of second phases and off-stoichiometric compounds that appear in the final microstructure. This effect can clearly be seen in figure 1. Samples low in Nd possess at least 7 different phases in the post-processed material over a range of 150 degrees. Samples high in Nd possess only 4 different phases in a range up to 400 degrees. Hence, Nd is a 1:2:3 stabilizer.

#### The Need for Microgravity Experiments

The difficulties of processing these materials in one g present a clear case for microgravity processing. For example, the large density differences in these multi-component systems cause sedimentation in the melt. Also,  $YBa_2Cu_3O_{7-\delta}$  and rare earth (RE) substituted  $YBa_2Cu_3O_{7-\delta}$  have a very low thermal conductivity, such that moderate heating and cooling rates develop large thermal gradients in the melt, thereby driving convection. Furthermore, these materials react with all known containing media, but the poor electrical conductivity at room temperature prevents the use of more conventional electromagnetic containerless processing techniques. For various reasons, other techniques for containerless processing are not appropriate because control of the processing environment is crucial to maintaining oxygen stoichiometry and preventing contamination by other gasses such as  $CO_2$ . Furthermore, heat capacity, viscosity and surface tension measurements on the undercooled liquid melt cannot be done on earth but can be obtained in microgravity. Fundamental studies of the melting, undercooling, and solidification behavior under the highly controlled conditions possible in a microgravity environment will lead to a greater understanding of these materials. In addition, it will be possible to produce benchmark materials in space.

#### Future Work

Containerless melt processing has proven to be a novel technique for gaining valuable information about the phase relationships in oxide superconductor systems. In particular, the techniques put forth in this study allowed for obtaining information unavailable using conventional processing methods due to the avoidance of any container contamination effects.

Experiments are planned to continue the fundamental high temperature phase relationships using the 2-meter drop tube at Vanderbilt. In addition, aero-acoustic levitation experiments will be performed on 2.5 mm drops to determine the viability of this technique for ground based containerless processing on these systems.

An additional goal of this program is to develop collaboration with other groups and provide access to the unique processing strategies developed by the microgravity program. Ultimately this research effort will lead to a proposed flight experiment where investigators from industry,

national laboratories, and universities could participate in highly controlled experiments on the melting and solidification behavior of oxide superconducting systems.

### References

1. R.W. McCallum, M.J. Kramer, T.J. Folkerts, S.R. Arrasmith, B.D. Merkle, S.I. Yoo, Youwen Xu and K.W. Dennis, *Containerless Melt Processing of REBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> {RE=Y, Gd, Nd} High Temperature Superconductors*, in Physical and Materials Properties of High Temperature Superconductors, S.K. Malik and S.S. Shah eds. (Nova Science Publishers, Inc. 1992) p. 667.
2. R.S. Roth, K.L. Davis and J.R. Dennis, *Adv. Ceram. Mater.* **3B**, v. 2, (1987) 303.
3. K. Osamura and W. Zhang, *Z. Metallkunde* **82**, (1991) 408.
4. J.K.R. Weber, D.S. Hampton, D.R. Merkley, C.A. Rey, M.M. Zatarski, and P.C. Nordine, *Ceram. Bull.* **70**, 71 (1991).
5. J.R. Olive, W.H. Hofmeister, R.J. Bayuzick, G. Carro, J.P. McHugh, R.H. Hopkins, M. Vlasse, J.K.R. Weber, P.C. Nordine, and M. McElfresh, *J. Mater. Res.* **9**, no. 1, 1 (1994).

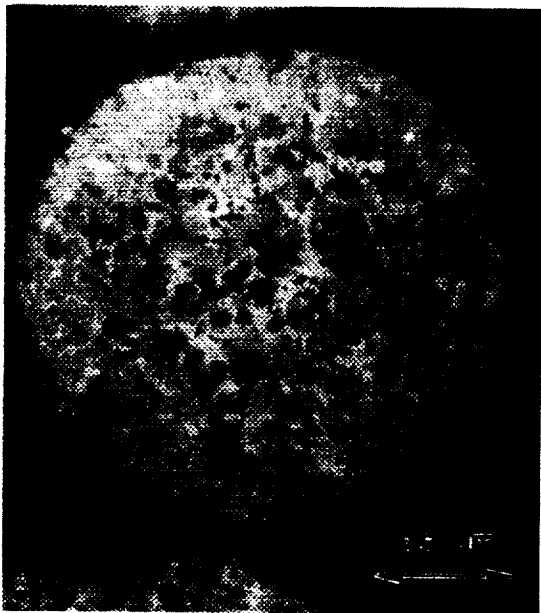


Figure 2. Micrograph of a Y-1:2:3 sample processed in pure O<sub>2</sub> at 1775 °C in the drop tube indicating incomplete melting.



Figure 3. Characteristic micrograph of Y<sub>8</sub>Nd<sub>2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> processed in pure O<sub>2</sub> at 1775 °C in the drop tube.

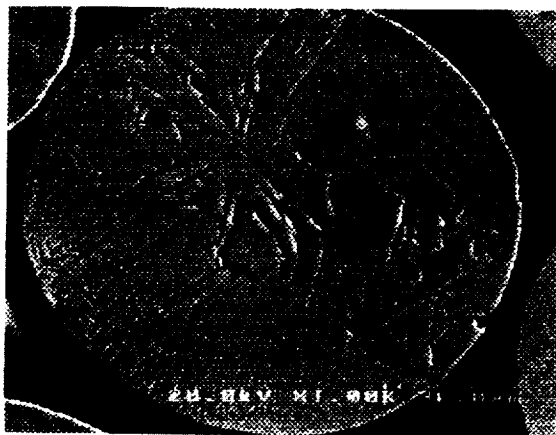


Figure 4. Micrograph of Y<sub>3</sub>Nd<sub>7</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> processed in pure O<sub>2</sub> at 1675 °C in the drop tube showing primary RE-1:2:3 solidification.

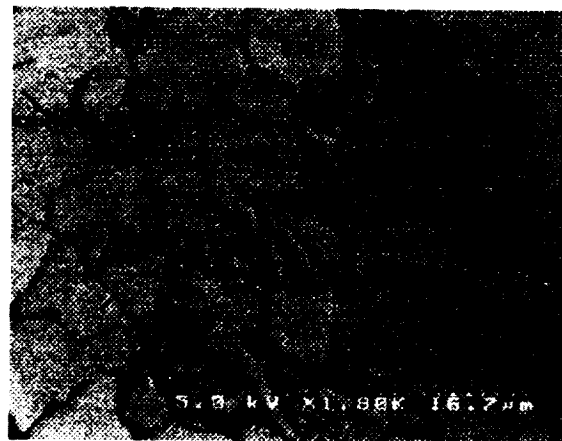


Figure 5. Micrograph of Y<sub>5</sub>Nd<sub>5</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> processed in pure O<sub>2</sub> at 1725 °C in the drop tube. The lighter dendritic phase corresponds to 2:2:3.