Abstract

The Ndl-xBa2-xCu3O7+y system has been shown by a number of investigators to exhibit a solid solution for x=0 to x=0.5 for temperatures above the orthorhomic to tetragonal transition of the x=0 end point. Published measurements of the superconducting properties as a function of x have not yielded a consistent behavior of transition temperature upon composition. While x-ray diffraction and TGA measurements are generally performed on powdered samples, superconductivity measurements are performed on sintered compacts. D.C. Magnetization measurements of sintered compacts have shown that the transition width and superconducting fraction is strongly dependent on the temperature at which the material is sintered. Scanning Auger Microscopy (SAM) of fracture surfaces of sintered samples have shown that even in very high purity samples a thin Nd deficient grain boundary layer exists. Hysteresis measurements show good intergranular critical currents at high fields but the intragranular critical currents are still low.

Introduction

NdBa2Cu3O7 exhibits both a higher peritectic decomposition temperature and a broader range of primary solidification for the 123 phase than YBa2Cu3O7. In addition unlike YBa2Cu3O7, the low temperature orthorhombic phase exists over a range of Nd compositions with little effect on the transition temperature. From a processing standpoint these factors should make Ndl-xBa2-xCu3O7+y an interesting alternative to YBa2Cu3O7 for applications. In addition to easing some processing constraints, the substitution of Nd onto Ba sites may have the added benefit of introducing enhanced pinning of magnetic flux due to variations in the local oxygen order.

In practice it has proven to be more difficult to obtain sharp transition temperatures in the Nd compound than in the Y material. Numerous authors have reported on the solid solution Ndl-xBa2-xCu3O7+y existing between the Nd2Cu3O7+y and the Nd3Ba3Cu5O7+y compounds based on x-ray diffraction data. However there is considerable disagreement in the literature as to the superconducting properties as a function of Nd content based on resistivity and ac susceptibility measurements. Common to most of the literature studies is a decrease in the Meissner fraction as the Nd content is increased. D. C. Magnetization measurements of sintered compacts have shown that the transition width and superconducting fraction are strongly dependant on the temperature at which the material is sintered. For small batches (5 g) in which sample homogeneity can be assured, sharp transitions are now easily obtained over the range of superconducting compositions. In larger batches (50 g) we have seen that small inhomogeneity in the precursor powder before calcining results in significant impurity phases. For samples with x>0, this results in broad transitions. In this work we present results which bear on the origin of the broad transitions when sample homogeneity appears not to be a problem and we present magnetization data showing the temperature and field dependence of a sample with x=0.04.

Experimental Details

The materials for this study were prepared by low temperature calcination of Nd2O3, BaCO3, and CuO. The precursor powders were dried, weighed and ground together in a micromill to submicron size. The materials were pressed into pellets and calcined twice at 890 °C in an air flow of 10 liters/minutes for 24 hours with an intermediate grinding and pressing. Compositions Ndl-xBa2-xCu3O7+y were prepared either directly from the starting constituents of by micronilling calcined powders with x=0 and x=0.5. Samples with sharp transitions and consistent Meissner fraction (Fig. 1) were prepared using the following final schedule. In O2 the samples were ramped rapidly to 900 °C and held for 30 minutes followed by ramping to 1050 °C where they were held for 24 hours. The temperature was then decreased at 0.1 °C/min to 900 °C and held for 1 hour, followed by cooling at 0.5 °C/min to 600 °C with a pause of 6 hours. Following a ramp at 1 °C/min to 400 °C, the samples were held for 24 hours and furnace cooled. All samples appeared single phase as determined by x-ray diffraction. Detailed examination using optical and Scanning Electron Microscope (SEM) as well as Differential Thermal Analysis (DTA) revealed impurity phases in some samples. Using Energy Dispersive X-ray Spectroscopy (EDS) on polished cross sections showed that independent of preparation route, the Nd and Ba were uniformly distributed in the primary phase.

Figure 1. Superconducting transition temperature versus composition for (a) Ndl-xCa0.5Ba0.5Cu3O7+y and (b) Ndl-xBa2-xCu3O7+y solid solutions. 10, 50 and 90 % of the transition is measured by DC magnetization are indicated.

Magnetization measurements were performed in a Quantum Design MPMS SQUID magnetometer both in field cooled and zero field cooled mode. As x is increased the transition temperatures and widths indicate a number of regimes(Fig. 3). For 0<x<0.02 the systematic decrease in the transition width and the varying Meissner fraction suggest that despite the normal x-ray diffraction patterns these samples are not single phase. Close metallographic examination using both optical and Scanning Electron microscopes confirmed this conclusion. The source of the impurity was traced to the fact that the starting Nd2O3 powder was dried at 750 °C which is below the decomposition temperature and a broader range of primary solidification for the 123 phase than YBa2Cu3O7. In addition to

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Subsequent drying of the Nd$_2$O$_3$ for 24 hours at 950 °C resulted in a 1.25% weight loss. Thus for $x < 0.0125$ the samples are Nd deficient showing that the range of solid solution does not extend beyond the 123 compound. For 0.02 $< x < 0.3$ the superconducting transitions are sharp and exhibit constant Meissner fraction. There is evidence for two plateaus in the data, the first at 90 K for $x < 0.1$ and the second at approximately 50 K for 0.1 $< x < 0.3$. The $x = 0.3$ sample shows a sharp transition at 35 K but only 1/3 the Meissner fraction of the other superconducting samples. For compositions $x = 0.4$ and $x = 0.5$ the magnetization data follows a Curie law at low temperatures with the 0.4 sample showing evidence of 2% of a superconducting impurity phase at 20 K. Careful examination of the x-ray diffraction patterns show that for $x < 0.1$ the material is orthorhombic and for $x > 0.3$ it is tetragonal. For 0.1 $< x < 0.3$ there is some evidence for splitting of the tetragonal x-ray diffraction lines suggesting that the analogy to the YBa$_2$Cu$_3$O$_y$ system is correct with the ortho I, ortho II, and tetragonal phases. As is expected in this situation, the width of the superconducting transitions reflect the slope of the $T_C$ versus $x$ curve. For comparison samples of nominal composition Nd$_{1.25}$Ca$_{1.75}$Cu$_3$O$_7$ prepared. Since Ca$_{2+}$ has the same ionic radius as Nd$_{3+}$, substituting Ca for Ba should introduce the same degree of size effect without the change in O content associated with the valence change. While the Ca substitution does effect $T_C$, the depression is not nearly as pronounced as in the Nd case.

While the above data is well behaved, it was observed that the transition widths, Meissner and screening fractions for all values of $x$ are much more dependent on processing parameters than in the Y case. In an attempt to understand the origin of the broad transition widths and inconsistent Meissner fractions obtained under normal Y processing conditions a wide range of processing conditions were investigated for the composition Nd$_{1.25}$Ba$_{1.75}$Cu$_3$O$_y$. It was determined that samples which were furnace cooled from 1000 °C to 900 °C prior to oxygenation exhibited the same broad transitions as samples quenched from 1000 °C and then heated to 900 °C prior to oxygenation. Extended anneals (up to 96 hours) at 450 °C did not appreciably affect the shape of the transitions. When annealed at 450 °C for 16 hours in N$_2$ the weight loss for the slow cooled sample with the sharp transition was twice that of the normally processed material. When the sintering temperature was raised to 1050 °C, a marked change in the behavior was noted. Independent of the heat treatment intermediate between sintering and the final 450 °C anneal, the samples exhibited consistent transition temperatures with uniformly sharp transitions and high Meissner fractions.

Interestingly when a sample with a sharp transition was subsequently heated to 1000 °C for 24 hours and oxygenated normally the sample exhibited a broad transition. This is in contrast to the sharp transition obtained when after sintering at 1050 °C and cooling to 1000 °C holding for 24 hours and then oxygenated normally. It should be noted that the peritectic decomposition temperature of Nd$_{1.25}$Ba$_{1.75}$Cu$_3$O$_7$ is $\sim 1110$ °C in O$_2$ so that no decomposition of the compound should take place during the 1050 °C sintering. Since a single sample was changed from a sharp transition to a broad transition, the transition width is not associated with sample inhomogeneity due to initial preparation but rather with the sintering temperature itself. Differential Thermal Analysis (DTA) of two samples, one sintered at 1000 °C with a broad transition and the other at 1050 °C with a sharp transition revealed the presence of a minor melting event at 974 °C in both samples. The event is tentatively identified as the P1 reaction and indicates the presence of less than 1 wt% impurity phase.

With a minor melting event taking place near the region of interest, the possibility of the distribution of the impurity phase affecting the oxygenation of the sample exists. In order to investigate this hypothesis, a broad and a sharp transition sample were fractured in situ in a Scanning Auger Microscope (SAM). In both samples a thin Nd deficient grain boundary layer was found. The thickness of the layer was the same within experimental resolution. In both samples the oxygen content was uniform within individual grains. Due to sample orientation effects comparison of oxygen content between grains was not accurate enough to determine overall oxygen homogeneity. No evidence was found to support the initial hypothesis.

A second hypothesis that is currently being investigated is that Ca on the Nd sites is responsible for the broad transition. The lower site disorder at higher temperature could result from what is effectively more reducing atmosphere at high temperature. The effect of O$_2$ partial pressure on transition width is currently being investigated for Nd$_{1.25}$Ba$_{1.75}$Cu$_3$O$_7$. When the O$_2$ partial pressure is reduced to 1% in Ar at 940 °C the sample decomposes into Nd$_2$BaCuO$_7$, Nd$_2$BaCu$_2$O$_5$ and CuO. If this decomposition can be controlled, it can be used to produce pinning sites in a manner analogous to that of the decomposition of YBa$_2$Cu$_3$O$_y$.

![Figure 2. Magnetization versus Temperature for Nd$_{1.04}$Ba$_{1.96}$Cu$_3$O$_7$](image-url)

For the sample $x = 0.04$, field cooled magnetization versus temperature measurements show a sharp transition (Fig. 2). In addition the small anomaly below $T_C$ is associated with a non-equilibrium flux distribution trapped in the sample during cooling. The zero field cooled data shows field starting to penetrate the sample at 40 K indicating weak link behavior. High field hysteresis measurements were carried out at 10, 30, 50, and 70 K (Fig. 3). Two factors are immediately apparent in the magnetization loops. First is the paramagnetic contribution of the Nd moments which increases at low temperature. Second is the marked "fish tail effect" at all temperatures above 10 K. Extensive work on this effect in single crystals of YBa$_2$Cu$_3$O$_7$ has shown that it is due to incomplete oxygenation of the sample. Upon extended oxygen annealing the effect is eliminated and the width of the loop and hence $J_C$ is considerably enhanced. If the optimum anneal is exceeded, $J_C$ is
reduced from the optimum value. If the analogy to the Y material holds for Nd, further oxygen annealing is necessary before we can separate the effect on pinning of Nd on the Ba sites from oxygen defects due to insufficient heat treatment.

In Figure 4, the width of the hysteresis loop versus field is plotted for all four measured temperatures. Of particular interest is the relative field independence of the high field grain size of 20 microns gives critical currents of 10^6, 4x10^5, and 4x10^4 amps/cm² for 10, 30, 50, and 70 K in an applied field of 3T. These values are very encouraging considering the incomplete oxygenation of the sample. The situation on the grain boundaries is considerably less positive. Due to the high temperatures required to obtain sharp transitions, grain growth is a problem even in very clean samples. The microcracking which is expected to occur with grains of this size combined with the observed Nd deficient layer on the grain boundaries results in very low critical currents and considerable effort will be required to overcome these problems.

Conclusions

Nd_{1-x}Ba_{2-x}Cu_3O_7+d samples have been prepared with sharp superconducting transitions by careful attention to the details of sample preparation. Two causes for broad samples have been observed. The first is sample inhomogeneity which is more difficult to eliminate than in the YBa_2Cu_3O_7 case and the second appears to be associated with site disorder within a homogeneous sample. Very reasonable intragranular critical currents have been obtained in a sample with a small amount of Nd substituted on the Ba sites but it is not clear if the Nd

Figure 4. Width of the magnetic hysteresis loop for Nd_{1.04}Ba_{1.96}Cu_3O_7+d as a function of applied field.

plays a direct role in flux pinning at this time. Intergranular critical currents are still quite low due to the large grain size in the high temperature processed material and the Nd deficient layer on the grain boundaries.

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References