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The occurrence of superconductivity in the mixed yttrium-terbium, barium copper oxide ceramics

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This is to certify that the Master's thesis of

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has been approved by the Examining Committee for the thesis requirement for the Master of Science degree in Physics at the December 1987 graduation.
To my father who thought it would be
nice to have yet another JEK thesis in
the physics library.

And to my mother who put up with it.
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The Vice-President for Research and Educational Development and the Dean of the Graduate College, Dr. Spriestersbach, is acknowledged for providing a modest starter grant for materials and supplies.
This study reports the effect of terbium substitutions for yttrium in $Y_1Ba_2Cu_3O_{7-\delta}$ on the resistivity as a function of temperature. Samples of $Tb_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ for $x = 0, 0.04, 0.08, 0.12$ and $0.16$ were studied. Mixtures of $x = 0, 0.04, 0.08$ and $0.12$ were prepared by the citrate method and were sintered at $945 \degree C$ for 20 hours, slow cooled to $300 \degree C$ and then removed from the furnace. Since the $x = 0.12$ sample reacted with the alumina boat, a second $x = 0.12$ and an $x = 0.16$ sample were sintered at $910 \degree C$ after which there was no visible sign of any reaction between the samples and the boat. All of the samples were oxygen annealed at $940 \degree C$ for two and a half hours and then at $555 \degree C$ for three hours. They were then furnace cooled to about room temperature.

A current of $6 \text{ mA}$ was used in the resistance measurements. All of the samples displayed superconductivity at temperatures above $90 \text{ K}$. There appeared to be no systematic effect of the terbium substitution on the transition temperature. There was a minimum in the normal state resistivity for $x = 0.08$.

These results are compared to a similar study where cerium was substituted for yttrium. They are also discussed in context of a study showing that bismuth additions had an effect on the resistivity similar to that reported here for terbium.
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INTRODUCTION

Superconductivity was discovered by Onnes in 1911 [1]. In the ensuing 75 years materials with critical temperatures, $T_c$, as high as 23.3 K have been discovered [2,3]. Recently materials with much higher critical temperatures were discovered.

Bednorz and Mueller discovered and reported evidence of transition temperatures of 30 K while studying the L-Ba-Cu-O system in early 1986 [4]. This discovery was confirmed in the fall of 1986 [5] and the superconducting compound $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ was shown to have a potassium-nickel fluoride structure [6].

Chu et al. in early 1987 [7] reported that under pressure this compound exhibited a superconductivity onset temperature of 52.5 K and zero resistance at about 25 K.

In March 1987 Chu et al. [8] reported superconductivity in the related $\text{Y-Ba-Cu-O}$ oxygen defect perovskite system at 93 K. The superconducting phase of the material was shown to have the composition $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (where $\delta \approx 0.15$) [9] and the structure shown in Figure 1 [9]. This compound will be referred to as the yttrium 123 compound.

This discovery has spurred a great deal of new interest in these materials. Theorists have yet to quantitatively explain the high transition temperatures [10,11]. Many groups are exploring possible tech-
nological applications and seeking to discover new physics from the
many compositional variations that exhibit superconductivity.

Since the discovery of high temperature superconductivity in
$Y_1Ba_2Cu_3O_7-\delta$ it has been shown that most of the rare-earths can be
substituted for the yttrium with little effect on the transition
temperature [for example 12,13,14,15,16]. However, total replacement
of yttrium by cerium, praseodymium and terbium removes the supercon­
ducting transition [12,13,16].

This is a report of a study of a partial replacement of yttrium by
terbium in $Y_1Ba_2Cu_3O_7-\delta$. The dependency of the transition temperature
and the resistivity for the substitutional compounds of
$Tb_xY_{1-x}Ba_2Cu_3O_7-\delta$ for $x = 0, 0.04, 0.08, 0.12$ and $0.16$ was determined
as a function of $x$. Comparisons are made with the results of Liang et
al. [17] for a similar replacement of yttrium by cerium.
CHAPTER I
THEORY AND WORKING EQUATIONS

Resistance and Resistivity

The resistance at any temperature can be found from Ohm’s law

\[ V = I R \]  \hspace{1cm} (i)

where \( V \) is the voltage across the sample, \( I \) is the current through the sample and \( R \) is the temperature dependent resistance of the sample.

It is typical of all these high temperature superconductors that as the temperature is decreased from room temperature the resistance drops in an approximately linear fashion. This region will be referred to as the normal portion of the resistivity. At a certain temperature the resistance begins to roll off smoothly downward. The resistance then drops abruptly to a very low value where the curve showing the relation then smoothly joins the zero resistance line for all lower temperatures. The sudden drop in resistance is the transition region and the zero resistance line is the superconducting region. This can be seen in Figure 2 for all the samples in this study. The broadened transition region can be due to many things, such as, different portions of the material becoming superconducting at different temperatures. Because these materials can have second phases and a
large number of grain boundaries due to the nature of the ceramic structure this spread in the transition temperature is not surprising.

There are three common forms for presenting this data. The ratio of the resistance at a given temperature to the resistance at room temperature can be plotted as a function of temperature. The ratio of the resistance to the normal state resistance as a function of temperature can also be graphed. Both of these methods eliminate geometric factors from the calculations. The latter of the two methods is used in this report and is discussed below. The resistance data can also be used to generate a graph of the intrinsic resistivity of the material versus temperature. In this form there are geometric factors to consider.

For a uniform parallelepiped the resistivity, $\rho$, is given by

$$\rho = \frac{RA}{L}$$

where $A$ is the cross sectional area through which the current flows and $L$ is the spacing between the contacts for measuring the potential drop along the length of the sample.

These ceramic materials have a porous nature due to the imperfect compacting of grains of the material. These particles are then fused in the sintering process to cause them to adhere but with some void spaces still remaining in the superconducting copper ceramics. Consequently equation (ii) does not yield the intrinsic resistivity of the compound if $A$ and $L$ are taken to be the outer dimensions.
There is currently no standard method reported in the literature for dealing with the effect of the porosity on the area and path length of the current in these materials. This report will not include a correction to the resistivity for possible effects of the porosity. The resistivity is an average value calculated for the fused grains of the compound with A and L determined from the external dimensions of the samples.

**Reduced Resistance**

A useful form for study of the transition is to plot the actual resistance divided by the normal state resistance for the same temperature. In this form any porosity correction is cancelled as are the geometric factors of sample size.

The normal state resistance would usually be measured by causing the sample to remain in the normal state at low temperatures by the application of large magnetic fields. These are estimated to be possibly 100 T or more for samples similar to those used in this study.

This laboratory does not have the requisite fields available so an alternate method is used. The linear region of the normal curve from about 140 K to 110 K (six to eight pairs of resistance and temperature) is fit with a line determined from a least squares fit. This line is then extended down through the transition region to give the expected normal resistance values. The correlation coefficients for these straight lines were .996 or larger.
A typical curve for these materials in this representation is S shaped. This is shown in Figure 3. The temperature at which the ordinate value begins to noticeably differ from the minimum detectable resistance is the zero resistance onset temperature. The transition region is crossed approximately linearly. The temperature at which the ordinate value begins to differ noticeably from one as the temperature is decreased from room temperature is the onset temperature.

**Thermal Emfs**

The resistance was determined from equation (i). However, since the mounting block was heated at one end there was the possibility of a thermal gradient along the sample. A thermal gradient would produce a thermal emf (called the Seebeck voltage) to be generated. Thermal emfs could also be produced by thermoelectric effects at the contacts or in the room temperature joints. These thermal emfs would be current independent and therefore their effect could be eliminated by averaging the resistance for the current applied in the forward and reverse directions [20]. These current directions were determined relative to their orientation with experimental probe. Therefore

\[
R_e = \frac{1}{2} \left[ \frac{V_f}{I_f} + \frac{V_r}{I_r} \right] \quad \text{(iii)}
\]

where \(R_e\) is the effective resistance, \(V_f\) and \(V_r\) are the measured forward and reverse voltages respectively and \(I_f\) and \(I_r\) are the forward
and reverse currents respectively. A sign convention for the current flow direction relative to the probe must be adopted and maintained.
CHAPTER II

EXPERIMENTAL APPARATUS

There were three apparatus used in the experiment: the apparatus to determine the temperature, another to determine the resistance of the sample, and another to determine the density of the sample.

**Temperature Measuring Apparatus**

A silicon diode (Lake Shore Cryotronics, Inc., Model DT-500DRC-B, Serial number D22201-B) was used in the forward bias mode as a thermometer. It was calibrated for a 10 $\mu$A current which was provided by a voltage divider adjusting a battery power supply [21]. The diode had separate leads for the current and emf test lines. A Leeds and Northrup K-4 potentiometer station (Leeds and Northrup Co., K-4 Potentiometer Type 7554) was used to measure the emf across a standard 1000 $\Omega$ resistor (James G. Biddle Co., Catalog number 601246, Serial number 34640) and thus the current to the diode by calculation. A Fluke multimeter (Fluke Inc., 8060A World Standard 4 1/2 Digit DMM with Frequency) was used to measure the emf of the diode.

**Resistance Measuring Apparatus**

The sample was mounted on a small sheet of fiberglass and held in place by phosphor-bronze pressure contacts with 0.4 cm long pieces of 16 gauge silver wire soldered with low temperature solder to their ends
to form line contacts as seen in Figure 4. The assembly was held in place on a copper block by two brass screws. The copper block was mounted with stainless-steel machine screws to a brass plate at the end of a thin-walled stainless-steel tube. Three 10 Ω 5 W carbon resistors that had been sanded flat on one side were epoxied to the end of the cooper block. These were wired in parallel to a Hewlett-Packard power supply (Hewlett-Packard Model 6200B) which was slaved to a variable 1.5 V DC battery voltage source to allow finer control of the current to the heater resistors. The temperature sensing diode was set in a hole in the copper block just behind the fiberglass sample mounting. A small amount of thermal compound (Wakefield Engineering, Inc., number 128) was used to insure good thermal contact while measuring the temperature of the block. The sample and copper block were surrounded by an aluminum box screwed to the brass plate as seen in Figure 5. A small amount of molecular sieve (Ultek Molecular Sieve, Ultek Division of Perkin Elmer Corp., Part number 31013500) was placed in the bottom of the box to trap moisture.

The sample current leads (the outer contacts in Figure 5) were wired in series with a precision 1 Ω resistor (Leeds and Northrup Co., Catalog number 4020-B, Serial number 1726357). The K-4 potentiometer was used to measure both the resistor emf (from which the sample current was calculated) and the sample emf (the inner contacts in Figure 5). The sample emf was measured in a four line contact configuration to remove the effect of lead resistances from the measurement. The
current was supplied by a voltage divider adjusting a battery power supply [21].

All of the wiring in the probe was 30 gauge wire-wrap wire. Figure 6 is a schematic of the electrical system.

**Density Measurement Apparatus**

The density was determined from the mass and volume of the sample. The mass was measured with a Mettler balance (Mettler Instrument Corp., Mettler Macro Balance, Model B5). The dimensions used to determine the volume, as well as the potentiometric lead spacing, were measured with a travelling microscope (Gaertner Scientific Corp., Serial number 3058P).
CHAPTER III
EXPERIMENTAL METHOD

Sample Preparation

The samples were made from the citrate chemical solution gel method in order to obtain a uniform and well mixed starting slurry [22]. The appropriate amounts of the nitrates of copper (Fischer Scientific Co., Certified ACS 99.7%), barium (Fischer Scientific Co., Certified ACS), yttrium (AESAR Johnson Matthey Inc., 99.9%) and terbium were mixed in a 100 ml Pyrex beaker with 25 to 50 ml of distilled water. The terbium nitrate was made by dissolving terbium metal in nitric acid in the same beaker that was to be used for the rest of the mixing. The dissolved terbium solution was dried on a hot plate under low heat before the nitrates were added. Next, 1.3 g of anhydrous citric acid (EM Science, 99.5%) and 1.1 ml of ethylene glycol (Mallinckrodt, analytic reagent) per gram of final product expected were added and the solution was agitated with a magnetic stirrer.

Heat was applied (while under a chemical vapor hood) until the solution began to react. This was evidenced by the emission of a red fuming nitrogen oxide gas. At this time the magnetic stirrer was removed and the hot plate was turned off. When there was no further evolution of red fuming nitrogen oxide heat was reapplied and the solution thickened to a gel.
The gel was then heated to dryness while stirring to prevent the formation of large clumps. When the resulting dry, dark powder reached a critical temperature the organics in the mixture ignited. No measurements of the temperatures involved in this process were made. The residual black powder was ground with a Coors high density alumina mortar and pestle for about 5 minutes.

The powder was placed in an alumina boat and heated for 4 hours at 790 °C in air. The temperature was measured with an uncalibrated chromel-alumel thermocouple with the reference junction at room temperature. Industry standards for thermocouple wire allow for the temperature determined by uncalibrated junctions to be in error by about 1 % in this temperature range [23]. It was felt that this amount of uncertainty still allowed the processing to be reproducible. The temperature appeared stable and accurate within 10 °C. The sample was removed, cooled and reground.

Flat discs were formed by putting about 1.5 ml of the powder in a 1/2'' diameter die. The die was put in a screw press and tightened to a torque of 80 ft·lbs. The dimensioned drawings of both the die and press are shown in Figures 7, 8. All of the discs formed were about 0.6 cm thick. The discs were then placed in alumina boats and heated for 20 hours at 945 °C in air in a Lindberg three zone tube furnace. The sample was slow cooled over a 4 hour span from a temperature of 945 °C to 300 °C.
The discs were attached to graphite supports with wax and cut with a diamond saw using a common synthetic kerosene as a lubricant. There were no signs of reaction with the fluid such as degradation or discoloration of the sample. Somewhat irregular samples roughly 1 mm x 1 mm x 10 mm were cut. Most of the residual wax was removed by touching the samples to a heated sheet of aluminum foil and some additional light scraping.

The samples were then placed in platinum boats and put in a quartz tube in a clamshell furnace. Oxygen gas was passed over the samples at a rate of about 190 ml per min. This was determined by measuring the volume of gas caught during a 30 second time interval in an upsidedown beaker held under water. The samples were heated from room temperature to about 940 °C where they were held for about two and a half hours. The samples were slow cooled to 555 °C and held there for three hours. The furnace was then shut off. The temperature was monitored with an uncalibrated chromel-alumel thermocouple with the reference junction in a mixture of distilled water and ice. The voltage of the thermocouple was recorded with an IBM personal computer. The samples and furnace were slow cooled over a 4 hour period to near room temperature. The oxygen was shut off and the samples removed. A white adherent ash of unknown composition was left on the side of the samples that had been attached with the wax during the cutting. As much ash was removed as possible and the sample was mounted so that the ash was not touching the contacts.
The processing for the entire series was completed in one week. The individual steps were done with little interruption. The 790 °C heating was done in one day with no adjustments of the furnace. The original five samples were fired together at 945°C. The \( x = 0.12 \) and \( x = 0.16 \) samples reacted heavily with the alumina boat. This is usually a sign that the sample will not become superconducting [24] so a second batch of each was prepared and sintered at 910 °C. All seven of the samples underwent the oxygen anneal together.

Mounting the Sample

The samples were mounted on the probe previously described. The silver contacts were lightly sanded and wiped clean. The probe was lowered about 4 cm into liquid nitrogen and left there until the boiling slowed. The aluminum box was then set about 1 to 2 cm above the surface of the liquid to reduce the thermal load to the heater resistors. Since there is a heat loss through the two stainless steel screws that mount the copper block and through the air that is in contact with the sides of the aluminum box, this small gap allows the heater resistors to operate more effectively. Although the aluminum box was not in contact with the liquid nitrogen, the probe would cool to 78 K. The rate of cooling at this location was almost as great as that of the probe in contact with the nitrogen.
**Temperature Settings**

The heater current was increased and the emf across the diode monitored. As the desired temperature was approached the current was reduced until finally the temperature appeared stable. The temperature typically drifted up slightly over the 2 to 4 minutes during which each datum was taken.

**Measuring the Temperature**

The temperature diode emf was measured and recorded before and after taking a datum. In each case the current through the 1000 Ω resistor was adjusted to 10 μA. The temperature had to remain stable for about a minute before the datum was taken. This stability indicated that a steady state of heat flow had been achieved.

**Measuring the Sample Emf and Current**

The emf and current across the sample were measured in the forward and reverse directions with the K-4 potentiometer. The current was calculated from a measured voltage across the standard 1 Ω resistor. It was about 6 mA for all of the samples.

**The Density Measurement Equipment**

The sample was weighed on a Mettler balance. The dimensions of the sample were measured as carefully as possible with the travelling microscope. Irregularities were measured and included in the volume determination.
CHAPTER IV
TREATMENT OF DATA

Calibration of the Temperature Sensing Diode

A calibrated silicon diode (Lake Shore Cryotronics, Model DT 500-DRC-B, number D22035-B) was used as the standard to calibrate the diode used in this experiment. They were both mounted in holes in the copper block with a little thermal compound. The probe was then run over the range 80 to 300 K. The calibrated voltage of the diode was measured before and after the working diode.

A sixth order polynomial fit was found to represent the calibration diode temperature voltage drop curve and was used to generate a table of emfs and temperatures for the second working diode. A sixth order polynomial was then developed for the working diode. The rms error for the curve for the working diode did not exceed 0.08 K [15].

Temperature Error

The error in the temperature was due to three main causes: the accuracy of the Fluke multimeter used to measure the diode voltage, the drift of the temperature noted above and the location of the thermometer. The instrument readings and the power supply fluctuations are random errors. The drift and location errors are systematic errors that could be eliminated by better equipment.
The Fluke meter has an accuracy of 0.04% of the reading plus 200 µV for the scale used. The diode emf was in the range 0.97 V near 78 K to 0.38 V near 300 K. This corresponds to a relative uncertainty of 0.07% and 0.10% in the respective voltages.

The typical drift in the diode emf as measured with the Fluke meter was 100 µV but was as low as apparently zero and as high as 300 µV. It is assumed that the data are taken at the average of the two temperature readings and that the drift correction is uncertain by 50 µV. This corresponds to relative uncertainties of 0.006% at 78 K and 0.02% at 300 K. There was a difference of a few microvolts at 78 K and about 40 µV at 300 K in the forward and reverse directions. This indicated a negligible thermal gradient at the low temperatures which increased with temperature. The difference in the end temperatures is unknown.

The fact that the thermometer was not in contact with the sample could lead to a systematically different temperature for the sample than that read by the thermometer. This difference is due to the gradient in temperature that must exist between the warmer copper block and the inner surface of the aluminum box that was at a temperature of about 78 K. This systematic error is estimated to be as large as several degrees near room temperature but negligibly small at temperatures less than 100 K.

The combined uncertainty in the voltage used to determine the temperature is then 0.08% at 78 K and 0.11% at 300 K. These voltage uncertainties correspond to uncertainties in the temperature of 0.3 K.
and 0.14 K respectively. With the error in the polynomial fit included, the uncertainties in the temperatures are 0.4 K at 78 K and 0.3 K at 300 K.

**Resistance Error**

The uncertainty in the measurement of the resistance was due to the uncertainty of the standard 1 Ω resistor and the uncertainty in the potentiometer readings. The standard resistor has a systematic error from its original calibration and a random error associated with room temperature fluctuations. The error in the readings was due to two factors: the uncertainty in the reading itself due to the limitations of the potentiometer and the variance of the voltages due to small fluctuations in the current. The latter were apparently due to convective air currents, aging effects on the batteries as a result of current drain on the power supply and the effect of the temperature fluctuations on the internal resistance.

The precision of the potentiometer was about 2 μV as described in the K-4 manual. The fluctuation variation was about 2 μV. These lead to a combined uncertainty in the voltage of 4 μV which corresponds to typical relative uncertainties in the voltages of 2% at the onset temperature and 1% at 300 K. The relative uncertainty in the current was then about 0.1%. Thus the resistances over the entire range are estimated to be uncertain by less than 3%.

The measurements of the voltages for forward and reverse currents were expected to result in slightly different values as a result of thermal emfs. The nature of the contact between the silver contacts
and the sample and the soldered joints in the circuit can result in positive or negative emfs. However, they were observed in only six sets. The usual behavior was to get a forward voltage of 1 to 2 \( \mu \)V and a reverse voltage of zero. This may be due some small unknown rectifying agent in the circuit or to a slight offset in the zero of the potentiometer itself. Since the few points that did show a sign change were bracketed by data that did not, all data that were forward (reverse) voltages of zero paired with values of up to 2 \( \mu \)V in the reverse (forward) direction were taken to represent an average sample emf of zero.

### Density Error

The Mettler balance was accurate to 0.05 mg. For the masses measured this corresponds to a relative uncertainty of 0.3\%. The uncertainty in the volume was dominated by the irregularities in the samples and is estimated to be 6\%. Most of this uncertainty was in the cross-sectional area of the sample.

### Resistivity Error

The uncertainty in the resistivity is estimated to be 15 \%. This is based on the combination of uncertainties in the quantities used to calculate the resistivity. This does not account for any systematic error in ignoring effects due to the porosities of the samples.
CONCLUSION

The addition of some Tb to \( \text{Tb}_x \text{Y}_{1-x} \text{Ba}_2 \text{Cu}_3 \text{O}_{7-\delta} \) has the following effects. It increases the density of the samples. This information is given in Table 1. There is an apparent minimum in the resistivity for \( x = 0.08 \). These curves are shown in Figures 9, 10, 11. The transition temperature is changed only slightly for \( x \leq 0.16 \). These data can be seen in Figure 12.

The original resistance curves of Figure 2 are misleading in that the ordering of the samples in descending resistance does not agree with that of the calculated resistivities shown in Figures 9, 10, 11. The resistivity curves clearly show that for \( x = 0.08 \) the normal state resistivity is a minimum.

Since the densities appear to increase as \( x \) is increased (Table 1), it is unlikely that only the density is responsible for the trend in the resistivity.

The reduced resistance curves of Figures 3 and 12 show that the onset temperatures have no systematic ordering. They also show a shift of about 1 K in the midpoint of the transition.

The resistivities have an uncertainty of 15%. This uncertainty is due mainly to geometric factors. The relative resistivities have an uncertainty of only the 3% associated with the resistance measure-
ments. The reduced resistance curves do not depend on the geometric factors and are thus uncertain by 3 %.

Since the x-ray data for the cerium 123 compound and that of the terbium 123 compound [19] are so similar it was speculated that the substitution of terbium in the yttrium 123 compound would lead to results similar to those of Liang et al.

Liang et al. showed that as the amount of cerium replacing yttrium in the sample was increased to 10 % the transition temperature dropped by 2 K. The drop in the transition temperature was 7 K for a replacement of 20 % of the yttrium by cerium. The same study showed that the normal resistivity went up as the amount of cerium in the compound was increased.

In the study by Liang et al. the starting powders were ground together in a crucible. The gel method used here is presumed to lead to a much finer powder with more intimate contact when compacted. It is unknown if the differences in the studies are due to a gel process effect or the grind and heat process or to some other cause. The cerium samples were multiphase. It is presently unknown if the samples in this study were single phase.

Frank et al. [25] report trends similar to those of Liang et al. for the Al$_x$Y$_{1-x}$Ba$_2$Cu$_3$O$_{7-\delta}$ system with 0 $\leq$ x $\leq$ 0.9. The samples in that study were produced from ground material and were multiphase. One of the phases was identified as the 123 structure.
Kilcoyne and Cywinski [26] report that in the $Y_{0.85}Bi_{0.15}Ba_2Cu_{0.75}O_7$ compound there is a reduction in the normal resistivity and little effect on the transition temperature. They also produced their samples by grinding the starting materials together. However, all forms of bismuth oxide melt below 900 °C as does bismuth metal. This led them to believe that it could behave like a flux enabling a more connected product to be formed. This increase in the connectivity of the sample was confirmed by electron microscopy and Kilcoyne and Cywinski claim that this increase was responsible for the normal resistivity drop. The samples in their study showed the presence of a small amount of a second unidentified phase.

The melting point of terbium oxide has not been determined. However, terbium metal melts at 1365 °C and thus is unlikely to become a flux. The mechanism that could allow the terbium to have an effect similar to that of bismuth is unclear.

The differences between terbium and the other metal substitutions could be due to the number of electrons shared. The different metals might substitute into different lattice sites in the perovskite cell or not into the cell at all.

The perovskite cell dimensions might vary with the insertion of the different metals. In the mixed Gd-Y 123 system, Tominga et al. [27] report slight cell dimension variations and no systematic variation in $T_c$. There is no presentation of resistivity data. They suggest that the $4f$ electrons are important to the behavior of the compounds in their study.
Ishida [28] reports for the mixed Yb-Er 123 system there was an effect on the $T_c$. The replacement of Er by Yb in the material lowered the transition temperature. There is no data on the resistivity presented. There was a shift in the cell dimensions for their single phase samples. It is also reported that some of the samples shrank during sintering. The shrinkage led to higher apparent densities and occurred for sintering temperatures just below those that caused reactions with the alumina boats. They report that samples sintered well below this temperature were visibly more porous.

In the present study the lower temperature sintering led to some of the largest densities and presumably the least porous materials. The differences between the porosities for the low temperature sinters in the present study and that of Ishida may be due to production related variables other than the compositions studied.

In conclusion replacement of Y by Tb in $\text{Tb}_{x}Y_{1-x}\text{Ba}_{2}\text{Cu}_{3}\text{O}_{7-\delta}$ leads to a minimum in the normal state resistivity for $x = 0.08$. $T_c$ shows little change for $x \leq 0.16$. It is unclear if the slight differences in $T_c$ are due to composition or to a random effect of processing. However, since the two samples with the lowest transition temperatures were also processed at the lowest temperatures, it is likely that the sinter temperature is responsible.

**Recommendations**

The first studies to follow this should be extending the terbium addition until the superconducting transition is removed. (A Tb 123 sample was made that did not show the Meissner effect. Therefore it is
felt that larger additions of Tb will eventually remove the superconducting transition.) Cerium, praseodymium and terbium should be compared when produced by the same processing methods. The processing should be optimized as much as possible. X-ray studies (which are already underway at The University of Iowa) and porosity studies should be performed. The compositional dependence of the critical current, susceptibility and Hall coefficient should be determined. These studies will allow characterization of the number and type of current carrier as well as the amount of the sample that is contributing to the superconducting state.
REFERENCES

1. H. K. Onnes, Leiden Comm., 120b, 3 (1911).
15. L. Martinson, Master's Thesis, University of Iowa, Iowa City, Iowa, unpublished.


24. L. Martinson, personal communication.


Table 1. The Densities of $\text{Tb}_{x}\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ for $x = 0, 0.04, 0.08, 0.12, 0.16$.

<table>
<thead>
<tr>
<th>Fraction of Tb, $x$</th>
<th>Mass Density, $\delta_a (\text{g/cm}^3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 (processed at 945 °C)</td>
<td>2.952</td>
</tr>
<tr>
<td>0.04 (processed at 945 °C)</td>
<td>2.636</td>
</tr>
<tr>
<td>0.08 (processed at 945 °C)</td>
<td>3.134</td>
</tr>
<tr>
<td>0.12 (processed at 945 °C)</td>
<td>5.183</td>
</tr>
<tr>
<td>0.12 (processed at 910 °C)</td>
<td>4.202</td>
</tr>
<tr>
<td>0.16 (processed at 910 °C)</td>
<td>4.294</td>
</tr>
</tbody>
</table>
Figure 1. The Oxygen Defect Perovskite Unit Cell for $Y_1Ba_2Cu_3O_7$. 
Figure 2. Resistance vs. Temperature for Various Tb Samples. The Samples are for the Series $\text{Tb}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. 

$x = 0.00$ (processed at 945 °C) •
$x = 0.04$ (processed at 945 °C) □
$x = 0.08$ (processed at 945 °C) ■
$x = 0.12$ (processed at 945 °C) △
$x = 0.12$ (processed at 910 °C) ▲
$x = 0.16$ (processed at 910 °C) ◆
Figure 3. Reduced Resistance vs. Temperature for Various Tb Samples. The Samples are for the Series Tb$_{X_{1-x}}$Y$_{1}$Ba$_{2}$Cu$_{3}O_{7.5}$.

- $x = 0.00$ (processed at 945 °C)
- $x = 0.04$ (processed at 945 °C)
- $x = 0.08$ (processed at 945 °C)
- $x = 0.12$ (processed at 945 °C)
- $x = 0.16$ (processed at 910 °C)
Figure 4. The Sample Holder. (About 6 Times Actual Size.)
Figure 5. The Probe. (About Twice Actual Size.)
Figure 6. The Circuit Schematic.
Figure 7. The Die. (About Two Thirds Actual Size.)
PLUNGER

HARDEN TO
BE TOUGH
NOT BRITTLE

1 1/2
1/2 DIA

EXTRA RELIEF
TO REDUCE
FRICTION

VERY SMOOTH
STAINLESS

1 1/4

BORE FOR
PLUNGER

STAINLESS

1/16

BASE

VERY SMOOTH

MAKE TWO

PLUNGER
BODY

BASE

POWDER
SAMPLE
LOCATION

MAKE ONE
BRASS

3/8

PUSHOUT
RING

A-087-062

SAMPLE PRESS

3/4 I.D.

3/4 I.D.

1 O.D.
Figure 8. The Screw Press. (About One Half Actual Size.)
Figure 9. Resistivity vs. Temperature for Various Tb Samples. The Samples are for the Series $\text{Tb}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. 

- $x = 0.00$ (processed at 945 °C) •
- $x = 0.04$ (processed at 945 °C) □
- $x = 0.08$ (processed at 945 °C) ■
- $x = 0.12$ (processed at 945 °C) △
- $x = 0.12$ (processed at 910 °C) ▲
- $x = 0.16$ (processed at 910 °C) ◊
Figure 10. Resistivity vs. Temperature for Various Tb Samples. The Samples are for the Series Tb$_x$Y$_{1-x}$Ba$_2$Cu$_3$O$_7$-$\delta$. (Expanded View.)

- $x = 0.00$ (processed at 945 °C)
- $x = 0.04$ (processed at 945 °C)
- $x = 0.08$ (processed at 945 °C)
- $x = 0.12$ (processed at 945 °C)
- $x = 0.12$ (processed at 910 °C)
- $x = 0.16$ (processed at 910 °C)
Figure 11. Resistivity vs. Temperature for Various Tb Samples. The Samples are for the Series \( \text{Tb}_x \text{Y}_{1-x} \text{Ba}_2 \text{Cu}_3 \text{O}_{7-\delta} \). (Expanded View.)

- \( x = 0.00 \) (processed at 945 °C) ●
- \( x = 0.04 \) (processed at 945 °C) □
- \( x = 0.08 \) (processed at 945 °C) ■
- \( x = 0.12 \) (processed at 945 °C) △
- \( x = 0.12 \) (processed at 910 °C) ▲
- \( x = 0.16 \) (processed at 910 °C) ◊
Figure 12. Reduced Resistance vs. Temperature for Various Tb Samples.
The Samples are for the Series $\text{Tb}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7-\delta$.
(Expanded View.)

- $x = 0.00$ (processed at 945 °C)
- $x = 0.04$ (processed at 945 °C)
- $x = 0.08$ (processed at 945 °C)
- $x = 0.12$ (processed at 945 °C)
- $x = 0.12$ (processed at 910 °C)
- $x = 0.16$ (processed at 910 °C)