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J. D. Vienna, U. Balachandran, W. Cermignani,† R. B. Poeppel,
and J. A. Taylor†

Materials and Components Technology Division
Argonne National Laboratory
Argonne, IL 60439 USA

†New York State College of Ceramics
Alfred University
Alfred, NY 14802 USA

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YBa₂Cu_(3-x)Co_xO_y -- A SUBSTRATE MATERIAL FOR YBCO SUPERCONDUCTORS

J. D. VIENNA,^{†*} U. BALACHANDRAN,[†] W. CERMIGNANI,^{*} R. B. POEPEL,[†]
AND J. A. TAYLOR^{*}

[†]Materials and Components Technology Division, Argonne National
Laboratory, Argonne, IL 60439 USA

^{*}New York State College of Ceramics, Alfred University, Alfred, NY 14802
USA

ABSTRACT

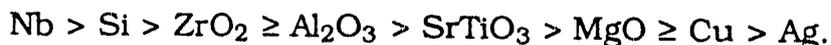
The physical properties of the ceramic YBa₂Cu_(3-x)Co_xO_y have been investigated in order to evaluate its usefulness as a substrate material for YBCO superconductors. YBa₂Cu_(3-x)Co_xO_y has been found to be thermally and chemically compatible with 123 and displays adequate electrical properties for a substrate material. A material with the nominal composition of YBa₂Cu_{7-7x}Co_{0.8x}O₇ was investigated, extensively. The mechanical properties of this material were found to be poor, e.g., tensile strength was only 60 MPa. A semiconductor-like behavior was observed with a room-temperature resistivity of 70 mΩ.cm and a resistivity equal to 4×10^6 mΩ.cm at 77K. [**Key words:** YBa₂Cu₃O_y, cobalt substitution, substrate, electrical properties, thermal properties, processing]

INTRODUCTION

A suitable substrate with acceptable properties that could be cofired with 123 superconductors would find uses in both electronics and magnetic field applications. Matching thermal expansions and sintering shrinkage would allow a composite to be densified without the formation of undue stresses. If this material is chemically compatible with 123, composites could easily be formed into complex geometries such as layered coils [1].

Chemical Compatibility

Many materials have been proposed as possible substrates for 123, but most have been found unsuitable due to reactivity with 123 or mismatches in firing shrinkage and thermal expansion. By nature, 123 is a very reactive (metastable) compound and decomposes when heated with a substrate. Cheung et al. has done extensive research on the reactions between 123 and common substrate materials. By comparing the percentage of remaining 123 after cofiring, the following reactivity scale was obtained [2]:



Cheung has suggested that the chemical interaction between 123 and

its substrate is controlled to a large extent by the highly electropositive Ba^{2+} ions reacting with the substrate and forming barium-rich compounds [2]. Komatsu et al. have studied several Barium rich substrate materials and found that $BaZrO_3$, Ba_2SiO_4 , and BaF_2 did not react strongly with 123, making them excellent candidates for substrate materials [3]. Dorris et al. have found that Y_2BaCuO_5 (211) is a chemically compatible substrate for 123 [4]. Due to large thermal mismatches, 211 is not suitable for coprocessing with 123.

Thermal Compatibility

It is important for a substrate material to be thermally compatible with the superconductor at high and low temperatures ($77\text{ K} \leq T \leq 900\text{ K}$). A thermal expansion (α) mismatch can cause cracks to develop in the superconductor. The coefficient of linear thermal expansion is listed in Table I for several common substrates.

Table I. Thermal properties for common substrate materials(25 - 800°C).

	123	MgO	SrTiO ₃	ZrO ₂	Al ₂ O ₃	Glass
$\alpha(10^6)$	16.9	13.0	11.1	10.3	7.0	5.0
T_m (°C)	1024	2852	2040	2700	2072	~1300

These materials (and others) do not form a satisfactory composites with 123 because of thermal mismatches. In order to closely match the firing shrinkage of a substrate material, both the 123 and substrate must sinter at the same temperatures and shrink the same amount.

EXPERIMENTAL PROCEDURES

$YBa_2Cu_{3-x}Co_xO_y$ was formed for a range of cobalt amounts ($0 \leq x \leq 1.5$). The precursors $BaCO_3$, Y_2O_3 , CuO , and Co_3O_4 were milled in methanol until an average particle size of 2 μm was achieved. The powders were then calcined at 900 °C for 12 h in flowing oxygen. A partial vacuum (3 torr) was used to increase calcination efficiency [5]. After phase identification by X-ray diffractometry (XRD), the calcined powders were ground by mortar and pestle and then pressed into 19 mm pellets at a pressure of 100 MPa. The pellets were then sintered in 1% oxygen (Balance nitrogen) at 870 for 12 h and annealed in high oxygen pressure (860 torr) for 12 h between 600 and 400°C [6]. Bars were cut to 4 x 3 x 15 mm and electroded with silver paint for four-point conductivity testing.

Precursors in the appropriate molar quantity to form $YBa_2Cu_{2.2}Co_{0.8}O_7$ were mixed with methanol in a polyethylene jar and milled until a mean particle diameter of 1.25 μm was achieved. The mixture was then dried by direct evaporation and calcined for 12 h in flowing oxygen at a temperature of 900°C and a pressure of 3 torr. The calcined powder was tested for phase purity and milled in methanol, pressed into 7 x 7 x 75

mm bars and sintered. After sintering, the bars were polished to 400 grit and broken in a four-point bend test.

RESULTS AND DISCUSSION

Routbort et al. has shown that Co^{3+} replaces Cu^{2+} on Cu(1) sites [7]. Because of the higher electropositivity of cobalt, additional oxygen is introduced. It has also been shown that Co-O-Co bonding occurs, causing localized phase segregation. This is confirmed by the lack of cobalt - copper ordering [8]. A tetragonal phase "pinning" occurs due to the addition and disordering of oxygen atoms in the Co-Cu-O plane (see Fig. 1). This transition occurs in localized areas, creating a two-phase mixture (orthorhombic and tetragonal). Scattered CuO_3 chains persist in the tetragonal phase until the cobalt concentrations becomes sufficiently high [8]. The O-T transition was seen to occur (by XRD) at a cobalt concentration of $x = 0.3$. This is in agreement with literature values [8][9][10].

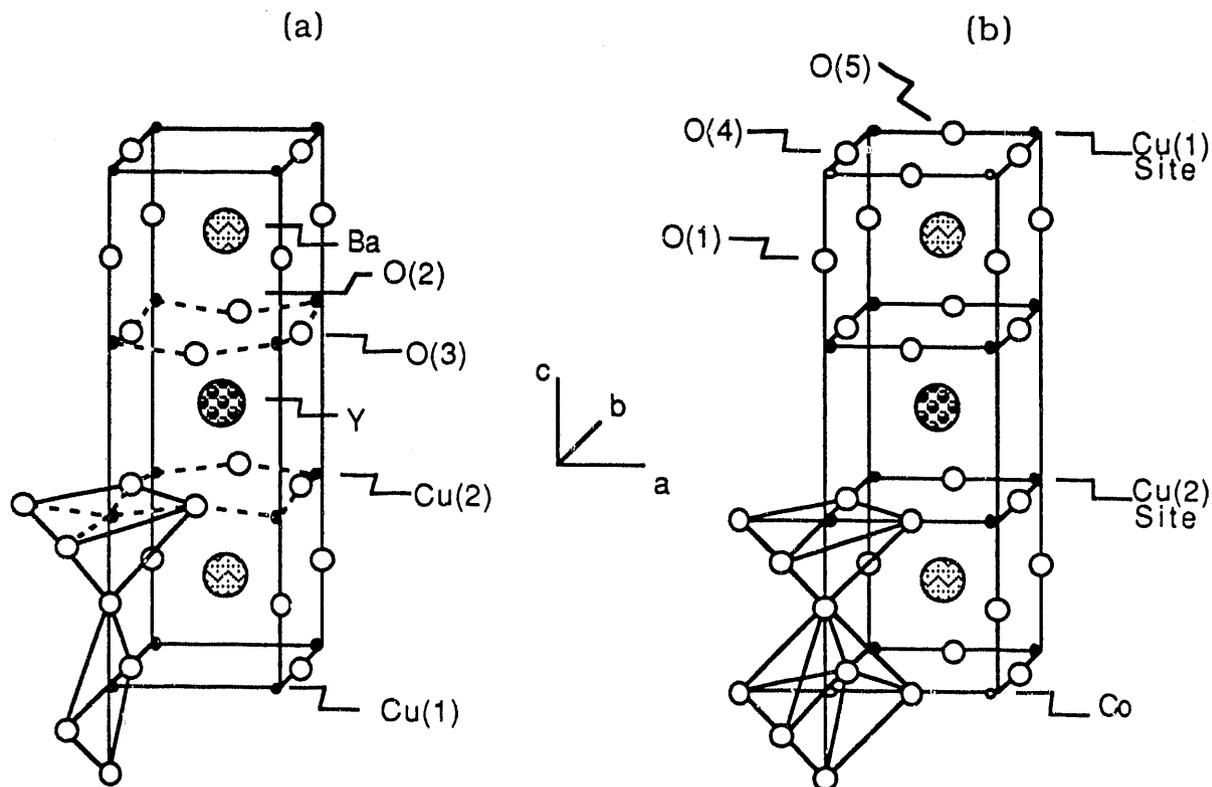


Figure 1. Structure of (a) orthorhombic and (b) tetragonal $\text{YBa}_2\text{Cu}_{4(3-x)}\text{Co}_x\text{O}_y$.

The solubility limit of cobalt in 123 is highly dependent on the processing parameters and has been reported to be as low as $x = 0.45$ [10] and as high as $x = 1.0$ [8]. In this work, a solubility limit of $x = 0.9$ was achieved. It is generally agreed that as the solubility limit is reached, CoO (or Co_3O_4), CuO , BaCuO_3 , and a Y-rich compound begin to form. These compounds can be seen by XRD and are confirmed by electron microscopy and DTA.

The critical temperature (onset) was found to decrease linearly with cobalt additions at a rate of $188 \text{ K}/x$ until $x = 0.5$, where the T_c could not be detected to a temperature as low as 20 K. Additional doping results in

increased resistivities at all temperatures. Figure 2 shows resistivity vs. temperature for $\text{YBa}_2\text{Cu}_{(3-x)}\text{Co}_x\text{O}_y$. The increasing resistivity with decreasing temperature is characteristic of semiconducting behavior. Aoki et al. has explained this ρ vs. T behavior as a result of hopping conduction of semi-localized carriers in the material [11].

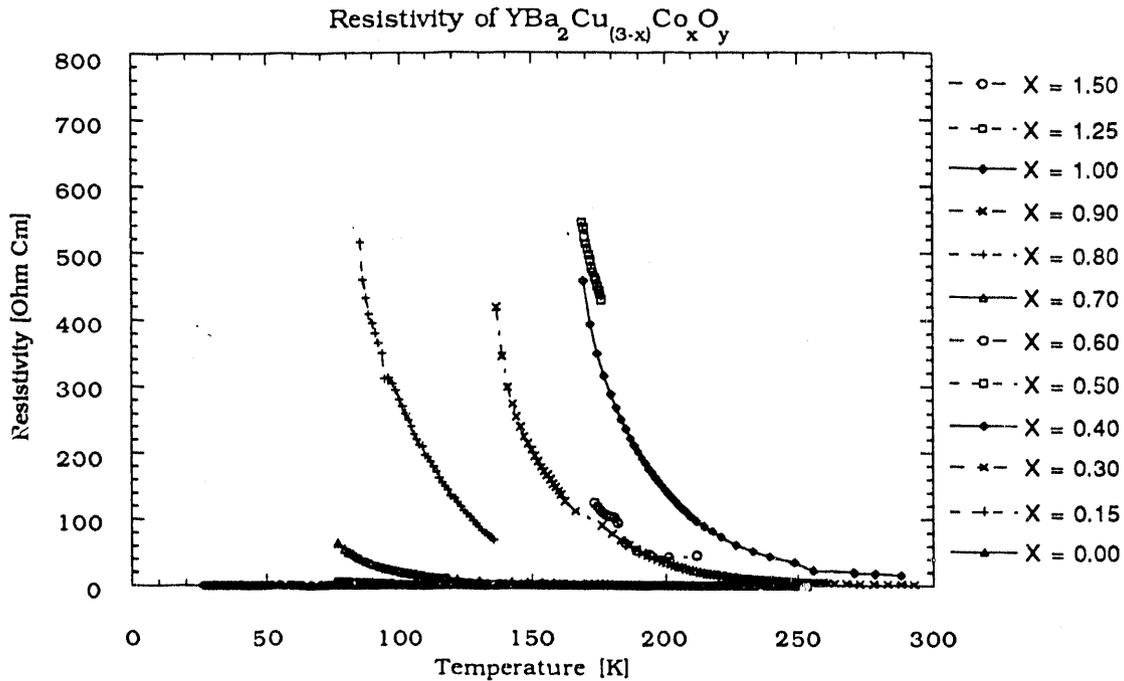


Figure 2. Resistivity of $\text{YBa}_2\text{Cu}_{(3-x)}\text{Co}_x\text{O}_y$ as a function of temperature for $0.0 \leq x \leq 1.5$.

The melting point of $\text{YBa}_2\text{Cu}_{(3-x)}\text{Co}_x\text{O}_y$ decreases linearly with cobalt concentration until the solubility limit is reached ($x = 0.9$). The rate's at which T_m drops were found to be $115^\circ\text{C}/x$, starting at 1035°C in oxygen, and $137^\circ\text{C}/x$ starting at 964°C in 1% oxygen (Balance nitrogen).

The linear coefficient of thermal expansion (α) was measured for $\text{YBa}_2\text{Cu}_{(3-x)}\text{Co}_x\text{O}_y$ in the range of 25 to 800°C in 1% oxygen. The thermal expansion for orthorhombic $\text{YBa}_2\text{Cu}_{(3-x)}\text{Co}_x\text{O}_y$ ($0 \leq x < 0.3$) was found to be essentially the same as that for 123. Above $x = 0.3$, $\text{YBa}_2\text{Cu}_{(3-x)}\text{Co}_x\text{O}_y$ is tetragonal and does not go through an O-T transition in the $500\text{-}700^\circ\text{C}$ range. The difference in thermal expansion between 123 and $\text{YBa}_2\text{Cu}_{(3-x)}\text{Co}_x\text{O}_y$ has been plotted (Fig. 3) by subtracting the normalized lengths (L/L_0) over the complete temperature range. $\text{YBa}_2\text{Cu}_{2.2}\text{Co}_{0.8}\text{O}_{7.0}$ and 123 deviate in thermal expansion only during the O-T transition, where 123 expands due to a disordering of oxygen in the basal plane.

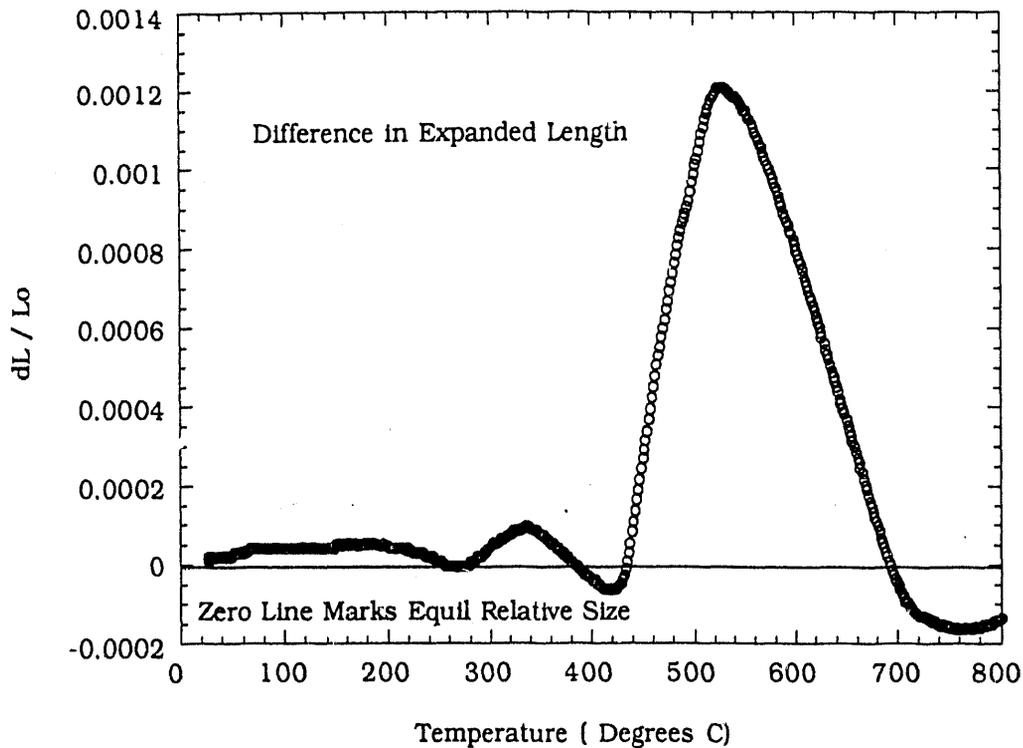


Figure 3. Linear thermal expansion mismatch of 123 and $\text{YBa}_2\text{Cu}_{2.2}\text{Co}_{0.8}\text{O}_{7.0}$.

Bars of $\text{YBa}_2\text{Cu}_{(2.2)}\text{Co}_{0.8}\text{O}_{7.0}$ were used to investigate the mechanical properties of this substrate material. A density of $5.71 \pm 0.2 \text{ g/cm}^3$ was measured for the bars by Archimedes method in ethanol at 25°C . The theoretical density of 662.7 g/cm^3 was calculated with a lattice volume of 176.13 \AA^3 [8] and an oxygen content of $y = 7.01$ (iodometric titration). These 91.4% dense bars were polished and broken in a four-point bend test. A flexural strength of $60 \pm 8 \text{ MPa}$ was measured. The low strength of this material is attributed to the very large grain size ($> 150 \mu\text{m}$) and low density. The elastic modulus (E) was measured by the ultrasonic velocity method at 163 GPa.

CONCLUSIONS

$\text{YBa}_2\text{Cu}_{(3-x)}\text{Co}_x\text{O}_y$ is an excellent candidate for a substrate material. Due to the similarity in composition and structure, this material can be coprocessed with 123 without cracking or strongly degrading the superconducting properties.

Diffusion of cobalt into the superconducting phase causes a degradation of superconducting properties near the 123 / $\text{YBa}_2\text{Cu}_{(3-x)}\text{Co}_x\text{O}_y$ interface (or more accurately, it causes a migration of this interface into the superconducting phase). Cobalt diffusion into the superconducting phase is consistent with the Fick's Law model and can be controlled by oxygen pressure, grain size and orientation, temperature, and time.

The thermal properties of this substrate are compatible with 123. The deviation in α occurs only at a tetragonal to orthorhombic transformation (see Fig. 3). High residual stresses can be avoided by cooling through this transformation very slowly.

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